

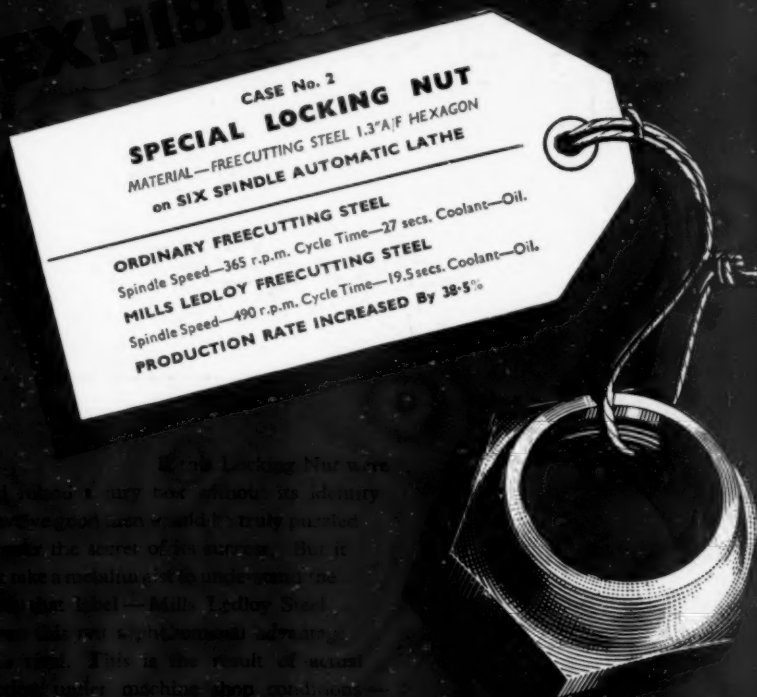
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THE BRITISH JOURNAL OF METALS

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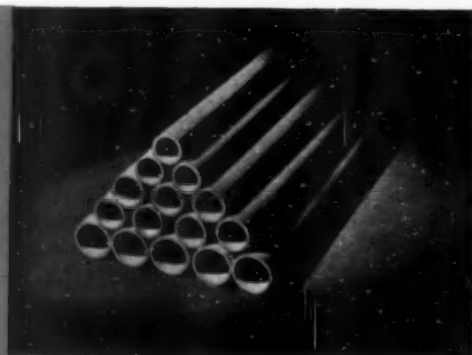
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# METALLURGIA

*The British Journal of Metals*

(INCORPORATING THE METALLURGICAL ENGINEER)

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# METALLURGIA

THE BRITISH JOURNAL OF METALS.

INCORPORATING "THE METALLURGICAL ENGINEER."

OCTOBER 1948

Vol. XXXVIII No. 228

## Steel and Politics

**I**N many respects it is a pity that the production of iron and steel in this country has become a subject for political controversy. So many statements are made by people with a political bias, but frequently with little or no knowledge of the industry, that it is difficult for laymen to separate the wheat from the chaff. It has been stated, for instance, that leaders of the industry can claim very little credit for its magnificent output record; that the only plan they have drawn up for modernisation would increase steel-making capacity by only a fraction of the pre-war figure; that the industry is about the tightest monopoly in the United Kingdom; that the tendency is to go slow on improvements in order to get profits from out-of-date plant as long as possible; that a minimum of 20 million tons of steel per annum is necessary to maintain full employment, but it is suggested that full employment is the last thing the industry wants. These and many other statements of a derogatory character make it very difficult to form an unbiased opinion on whether public control or public ownership of the iron and steel industry will, ultimately, be best for the country as a whole.

Few will deny that the workers and technicians in the industry have and are doing a great job of work, but this applies to all engaged in the industry and not least to organisation and leadership. Whether we like it or not, leadership is a virtue of industry and the real driving force behind all organisation; it demands the energy, will and enthusiasm to develop every material resource, actual and potential, of which any unit of industry is possessed. Only leadership and direction of the highest calibre have enabled the steel industry to push production toward peak level and to succeed, by an unswerving degree of control, in maintaining it there.

The plan for modernisation drawn up by the British Iron and Steel Federation in 1945 is still operating, but it was originally prepared as a basis for development; obviously the changing pattern of requirements and the changing possibilities of meeting these demands may necessitate adjustments to that plan. Assuming that the high level of employment continues to be maintained, a figure of 18 million tons has been agreed as a reasonable estimate of probable requirements in the early 1950's, following a recent Government examination of future steel demands. As pointed out in the current issue of the Federation's *Monthly Bulletin*, it is important not to over-estimate the level of future demand, partly because the computation is made on the basis of full employment, and there is always the risk of a considerable drop below the peak level, and also because the capital involved in expanding the steel industry is very large, so that it would be a grave mistake to lock up unduly large quantities of physical resources in such

an expansion when similar resources are needed for developing or modernising other industries, or for export.

The reference to monopoly is intended to convey that large profits were made by the steel industry during the inter-war years. During the seven years up to 1933 profits were abnormally low; the average return on capital in the industry did not exceed 2%, and between 1927 and 1936 about £50 million of capital was written off by the industry. The low profits were due to the fact that much of the plant was unused because the demand for steel was low. Even during this period however, according to the Balfour Report, "some subsequent investment of capital in the reconstruction and improvement of plant" had been given effect. Many schemes were started in 1932-33, which began to come to fruition from 1934 onwards. Up to 1938 some £50 million was spent on new plant. This period saw the coming into operation of new capacity at Corby, Ebbw Vale, Shotton, Scunthorpe, Cardiff and elsewhere. Through the Import Duties Advisory Committee, the Government exercised supervision over prices, so that there could be no question of the industry itself fixing prices in a manner which exploited the consumer. By 1939, the benefits of progress made in the preceding years were giving results and British prices, generally, were at least as low as those on the Continent and in America. This trend has become more marked in the post-war period when Continental prices, and to a smaller extent American prices, have risen above the British level.

With the exception of 1937, the steel industry has been working its plant during the last few years nearer to capacity than in living memory and to suggest that it is not anxious to promote conditions likely to maintain full employment is surely evidence that political views stretch the bounds of sanity. The striking fact is that the demand for steel is less stable than any other major raw material. This is supported by the Federation's *Bulletin* in which it is stated, that in the 1920's and early 1930's production of steel varied between 3.6 million tons and a peak of 9.6 million tons, while steel consumption fluctuated from a low point of 3.3 million tons in 1922 to 9.5 million tons in 1927 and then fell away again to 5 million tons in 1932. Violent fluctuations in steel production and consumption were not, of course, confined to this country. Thus, a minimum of 20 million tons capacity must bear some relation to the possible future demand for steel, further, capital investment on plant to ensure this increased capacity would be very considerable and would involve a great risk economically. A high consumption of steel, near to the plants capacity would mean economical working and low operating costs, but similar fluctuations in consumption as have been experienced in the past would mean uneconomical operation and high working costs. Obviously, therefore, a minimum production capacity of 20 million tons needs very careful consideration.

Since the formulation of the development plan in 1945, and its acceptance by the Government in 1946, more has become known about the fundamental economic problems which face this country and a clearer view on the probable trend of future events than was possible immediately after the termination of the war. The main changes in the position which bear on the demand for steel are summarised as follows:—

The recognition that it will be necessary for the country to rely to a greater extent on the export of machinery, vehicles and other products largely dependent on steel. Other claims involve the big programme of Colonial development and the expansion of oil production and refinement which have become pressing in the last few years.

These considerations, together with the assumption that a high level of employment will be maintained, have led to an agreed amount of 18 million tons as a reasonable estimate of probable requirements in the early 1950's. The broad schemes originally outlined in the Federation's plan was a capacity of 16 million tons, but the plants installed have almost invariably a larger capacity than originally allowed, while quicker melting has given a higher yield, as has continuous working of furnaces, which make for an output substantially in excess of 16 million tons. Indeed, it is claimed that the new developments may raise the capacity for the production of 17½ or possibly 18 million tons of steel by the early 1950's, although reservations are made concerning the growth of raw material supplies, in line with these production possibilities, and the regulation of imports. Past experience of the wide fluctuations of world steel prices means that a big risk factor is introduced with the latter. The risk of big imports in periods when demand for steel falls away is apparently being ignored. However, a new plan for the 1950-55 period will be necessary and a better knowledge of the economic conditions will be possible before such a plan is finally formed.

The most important point to remember, however, is not whether the steel industry is to be public controlled or public owned, but whether it is adopting the right attitude in developing the industry to meet present and future possible demands for steel at a low price. The evidence is convincing that the method at present on trial is proving a great success and it would seem unwise to change it simply to satisfy political ambitions.

### Iron and Steel Board Disbands

THE announcement that several members of the Iron and Steel Board had resigned would cause little surprise in iron and steel circles, although from many points of view it is unfortunate that the country will cease to have the services of very able men in a thankless task which they have carried out with marked success. The resigning members, Sir Archibald Forbes, the chairman; Mr. G. H. Latham and Mr. Richard Mather, nominated by the Iron and Steel Federation; and Sir Wilfred Ayre and Sir Alan Barlow, appointed by the Government to represent the interests of steel users and the public, felt that they could not remain on the Board during the period in which nationalisation of the industry was uppermost in the operations of the Government.

The Minister of Supply invited the Board to serve for a further year, but, apart from Mr. Lincoln Evans,

general secretary of the Confederation of Iron and Steel Trade Unions, and Mr. Ambrose Callaghan, president of the Blastfurnacemen's Union, they were unwilling to continue after completing their work on the outstanding major problems on which they are engaged. The Board has approved about two-thirds of the huge development and modernisation plan involving a capital expenditure of approximately £200 million. Meetings will continue to take place at intervals to the end of the year to deal with work that remains to be cleared up.

Since the appointment of the Board there has been comparatively smooth working between the Government and the industry, now that control has been taken over by the Ministry of Supply the Board's leadership will be sorely missed since the public control of policy for which it was responsible left enough responsibility to individual firms to ensure efficiency and initiative.

### Reorganisation of Hadfields

AS a result of increased commercial production and a widening of the range of the products of Hadfields Ltd., the Directors have been giving special consideration to the structure of the organisation with the object of developing still further the maximum efficiency in manufacture, economy in production and closer determination of cost. In addition, schemes have been approved by the Directors which may result in an expenditure, over the next five years, of over four million pounds.

The foundry is being reorganised, new plant being installed, both as regards replacement and expansion of business. A new forge is to be built and equipped with modern presses, together with heat treatment and ancillary facilities. The capacity thus provided will enable the Company to develop its production still further and ensure the supply of forged steel rolls. Both of the schemes have received Government sanction.

Probably the most interesting decision of the Board is the segregation of the undertaking into separate units, each owning its own land, buildings, plant and the like, and having its specialists concentrating their energies on the development of its own particular products. With this object, three new subsidiary companies have been created and came into operation on the first of the present month. These new subsidiary companies are:—

**HADFIELDS STEELS LTD.** which is responsible for the manufacture of steel of all kinds, including alloy and special steels and for the operation of the Company's large and small rolling mills producing billets, blooms and bars.

**HADFIELDS FORGINGS LTD.** which will continue to, develop the activities of the forging departments and the new forge when it is completed. Among other products the production of forged steel rolls is meeting with increasing success in replacing the importation of such rolls.

**HADFIELDS FOUNDRY AND ENGINEERING CO. LTD.** which is responsible for castings and the foundry development envisaged, part of which has already been accomplished.

The parent Company—Hadfields Ltd.—continues to act as the selling organisation for the entire output of the new subsidiary companies and the Board continues to control all matters of policy of all the units comprising the complete Group.

# The Sintering of Electrolytic Tantalum Powder

By Rupert H. Myers, M.Sc., Ph.D.\*

*The effect of temperature and time of heating on some properties of pressed electrolytic tantalum powder is described. The work was carried out to determine the best conditions for sintering in order to study the workability and recrystallisation phenomena of tantalum rod and wire made by the powder process. As a result of this work it has been possible to prepare a sintering schedule for electrolytic tantalum powder which has yielded bars suitable for mechanical working.*

## Introduction

IT is proposed to describe in this paper the effect of temperature and time of heating on some properties of pressed electrolytic tantalum powder. The method of preparing electrolytic tantalum powder and some of its properties have been detailed earlier.<sup>1</sup> The object of this work was to determine the optimum conditions for sintering so that a study could be made of the workability and recrystallisation phenomena of consolidated tantalum rod and wire.

The powder metallurgy technique of consolidating metal powders was chosen as the one most likely to be successful for tantalum, since vacuum fusion by induction heating, "vacuum arc" fusion and electrolytic deposition in a coherent form all presented very considerable difficulties.

## Pressing

There are two general methods available for pressing powders:—

- (1) Using a flexible container, e.g., rubber tube, a hydrostatic pressure being supplied by an external fluid.
- (2) Using hydraulic pressure where one or more punches are forced into a steel die containing the powder.

The latter method, being more generally applicable, was the one used in this work. By employing a specially constructed die it was possible to obtain side pressure as well as vertical loading with only one plunger. This die has been described in another paper.<sup>1</sup>

The pressing operation was required in this instance to produce a bar of tantalum which would be strong enough to enable it to be clamped firmly in the grips of the sintering furnace. Although tantalum is a soft metal, the softest of the refractory metals, considerable pressures were required to produce strong compacts. This was probably due to the fact that tantalum is coated with an unusually firm and coherent oxide film and a high pressure was needed to break it down and thus increase the area of metallic contact. Another possible reason was that the metallic particles were hardened by the absorbed gases which were present by virtue of the method of preparation of the powder. No trouble was experienced with slip cracks and no lubricant was used. It would appear that slip cracks, formed by a mass slippage of the powder on itself, tend to form more readily with harder metals than with

softer ones and usually where the particle size is comparatively small. This is particularly noticeable with tungsten and hard carbide powders where the particle size is usually less than 10 microns and frequently less than 1 micron compared with this tantalum powder which was of the order 50 microns. Furthermore, the individual particles of tantalum are much less porous than is the case with powders formed by hydrogen reduction of metallic oxides. Pressures of 50 tons per square inch and above were found to give bars which were strong enough for sintering. Most of the work was carried out with bars pressed at 50 tons per square inch but 80 tons per square inch was used in one series of experiments to provide a comparison of properties. Precautions were taken to produce evenly pressed bars. The most important step was to ensure that the powder was loaded uniformly into the die and carefully levelled. This was performed with a levelling device described earlier.<sup>1</sup>

## Sintering

The dimensions of bars used in this investigation were 3 to 5 in. long,  $\frac{1}{4}$  in. wide and  $\frac{1}{8}$  to  $\frac{1}{4}$  in. thick. They were heated in a vacuum of  $10^{-3}$  to  $10^{-4}$  mm. Hg pressure (as measured with a McLeod gauge) using a Nichrome wound furnace and a silica tube for temperatures up to 1,100° C. and the vacuum sintering furnace described in another paper<sup>2</sup> for temperatures up to just below the melting point. As well as causing the usual sintering of the pressed compacts, the heating in the case of tantalum served to de-gas the metal, this latter being essential for the production of very ductile metal. Because of the time taken for the absorbed gases and other impurities to diffuse out of the metal, longer sintering times were to be expected than was the case for tungsten or molybdenum. Vacuum pumps capable of maintaining high speed at low pressures were used to minimise the out-gassing time. Temperatures below 1,100° C. were measured with a chromel-alumel thermocouple and above this temperature a Cambridge type disappearing-filament optical pyrometer was used. All optical temperatures were corrected for non-black body conditions assuming an emissivity of 0.35.

## Effect of Temperature

In order to study the effect of temperature of heating on the sintering of tantalum, the properties density and electrical resistivity were chosen. In the first series of experiments bars pressed at 50 tons per square inch were employed and the sintering furnace was used for heating. Heating to each temperature was standardised at 30 minutes in a vacuum of  $10^{-3}$  to  $10^{-4}$  mm. Hg pressure

\* Commonwealth Research Officer, Baillieu Laboratory, University of Melbourne, Australia.

<sup>1</sup> Myers, R. H., *Proc. Aus. Inst. Min. and Met., N.S.*, 1946, **144**, 15.

<sup>2</sup> *Ibid.*, 1946, **144**, 45.



and density and electrical resistivity measurements were made after the bar had cooled to room temperature. The density was calculated from the weight of the bar and its volume, the latter being determined from the dimensions by measurement with a micrometer.

The electrical resistivity at 18°C. was determined using a Wolff pattern Kelvin Bridge with potential points about 1.5 in. apart. The dimensions of the bar were measured with a micrometer.

The results obtained are shown plotted as a function of temperature in Fig. 1. The change in weight of the bar is recorded as the change in weight per unit area of radiating surface since it was thought that, at the higher temperatures at least, this would give a better indication of the true value of the changes.

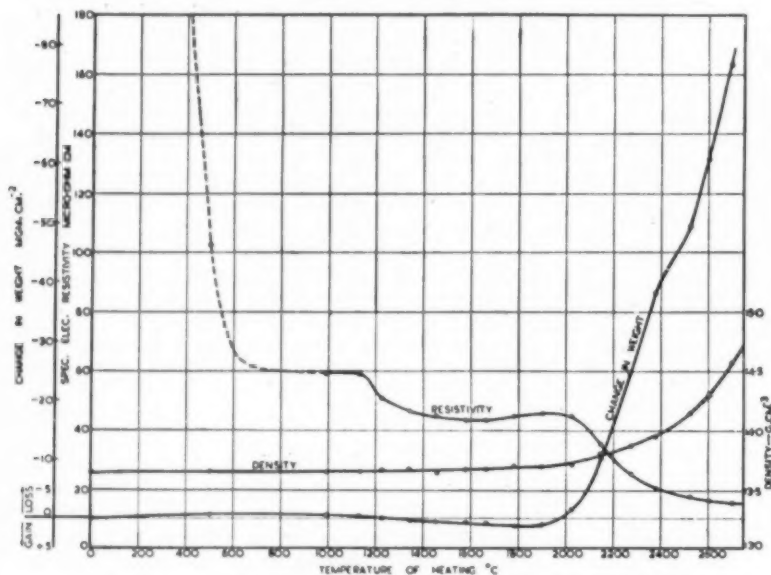


Fig. 1.—Curves showing the change in density, specific electrical resistivity and weight of pressed tantalum compacts after heating in vacuo for 30 minutes at various temperatures.

The specific electrical resistivity curve, Fig. 1, will be seen to fall rapidly at temperatures below about 600°C. and then remain steady up to 1,150°C. when another decrease occurred. This decrease was not maintained however, for, after heating to about 1,700°C., the resistivity increased, with a maximum between 1,900° and 2,000°C. and then began to fall again to an almost steady value after heating to 2,700°C. Because of the very large drop in resistivity after heating to temperatures below 600°C. it was decided to investigate the matter in more detail. Accordingly, a bar pressed at 50 tons per square inch and another, pressed at 80 tons per square inch for comparison, were heated in vacuo for 30 minutes at each temperature in a silica tube in a Nichrome wound furnace. The electrical resistivity was determined after each heating. The results, plotted as a function of temperature, are given in Fig. 2. The initial difference in resistivity of bars pressed at 50 and 80 tons per square inch gave an indication of the relative amounts of cold sintering which took place during pressing.

The density, which was less sensitive to changes occurring during heating of pressed compacts, showed,

when plotted as a function of temperature, that from about 1,600°C. there was a slight but steady contraction up to about 2,000°C. when the rate of increase in density rose steadily up to the highest temperature of heating.

The change in weight per unit area of radiating surface plotted against temperature of heating gave a

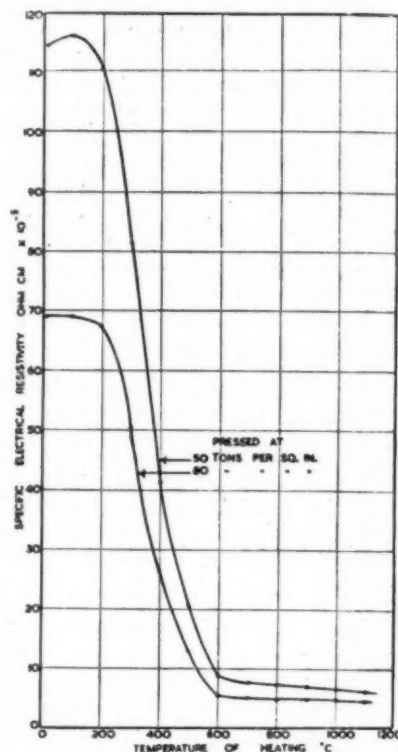


Fig. 2.—Curves showing the effect on specific electrical resistivity of heating, in vacuo, tantalum bars pressed at 50 and 80 tons per square inch.

complex curve. Points above the zero line represented a loss in weight while points below represented a gain in weight. Curves plotted with weight of bar and percentage weight loss of bar versus temperature were similar in outline. At the lower temperatures, below 2,000°C. they were almost identical, but at high temperatures the change in weight per unit area of radiating surface gave a better picture of the changes occurring.

In order to form some idea of what took place during the heating of tantalum compacts, it was necessary to consider the density, weight loss and the two resistivity (Figs. 1 and 2) curves together. After heating to 600°C. the resistivity fell from  $1,155 \times 10^{-6}$  to  $85 \times 10^{-6}$  ohm-cm., a very small decrease in weight was noticed and no measurable density change had occurred. It is known that the electrical resistivity of metals is particularly sensitive to the presence of impurities, particularly gaseous impurities, and it is for that reason that resistivity is not used more widely in the investigation of sintering phenomena. The fall in resistivity was thought to be due to the removal of certain impurities from the metallic particles which made up the compacts. Because of the very small loss in weight it



was suspected that the impurity removed may have been hydrogen. It was quite possible that hydrogen could be present in the tantalum powder because of the acid and alkali leaching which was carried out in its preparation. It was unlikely that the removal of hydrogen would affect the density and this was in accordance with the experimental data. In an endeavour to elucidate this point some tantalum powder was heated, *in vacuo*, to 650° C. in a silica tube. It was found that a gas was evolved and this was collected by displacement of oil from a glass tube inverted over the stream of bubbles coming through the oil in the rotary vacuum pump. The gas was found to be hydrogen. From a measurement of its volume at S.T.P. and knowing the weight of the tantalum powder which was heated, the following quantities of hydrogen were calculated to be present:—

1.0 ml. hydrogen (S.T.P.) per gram of Ta,  
i.e., 16 volumes of hydrogen per unit volume of Ta,  
i.e., 1.6 atomic per cent. hydrogen.

When no more gas was evolved at 650° C. (i.e., after 30 minutes) the temperature was raised to 700° C. However, no further hydrogen was evolved and it would appear that all of the absorbed hydrogen, which can be removed by low temperature heating *in vacuo*, may be removed by heating to temperatures of 600 to 650° C. Powder degassed in this fashion was then pressed into a bar at 50 tons per square inch and its electrical resistivity determined. This was found to be  $22.0 \times 10^{-5}$  ohm.-cm. compared with  $115.5 \times 10^{-5}$  ohm.-cm. when untreated powder was used. Thus the preheating treatment of tantalum powder prior to pressing accounted, in a large measure, for the resistivity drop. When the bar was heated to 650° C. the resistivity value obtained was the same as with bars pressed from untreated powder ( $7.5 \times 10^{-5}$  ohm.-cm.). These results supported the contention that hydrogen was mainly responsible for the low temperature changes which have been recorded in Figs. 1 and 2.

After heating to temperatures between 600° and 1,100° C., no change was found in any of the three properties measured. However, at about 1,150° C., significant changes occurred. The resistivity fell abruptly and the bar began to increase in weight. These results would at first sight appear to be conflicting since it has already been stated that the resistivity was sensitive to impurities and, from the increase in the bar weight, it was apparent that some impurity, almost certainly gaseous, had been absorbed. The resistivity, then, fell in spite of the contamination and this has been taken as meaning that sintering became appreciable at about 1,150° C.

As higher and higher temperatures were used it will be seen from Fig. 1 that the bar gained more and more in weight. The effect of the impurity finally outweighed the decrease in resistivity due to sintering and actually caused an increase in resistivity at about 1,900° C. This maximum in resistivity corresponded with the maximum gain in weight of the bar. It should be noted that the pressure inside the sintering bell before heating the bar was  $10^{-4}$  mm. Hg (as measured with a McLeod gauge) and was of the same order during the heating. Since the vacuum was kinetic, not static, it was thought that the hot tantalum absorbed one or more of the gases present even at the low pressures prevailing. It was unlikely that the resistivity increase was due to contamination by carbonaceous gases or vapours from the

diffusion pump oil (a water-cooled spiral vapour trap was interposed between the pumps and the heating system) for the following reasons:—

If carbon, or carbonaceous matter, were absorbed into the tantalum it would probably remain there up to and beyond the melting point of tantalum due to its affinity for that metal. Tantalum carbides, e.g., have melting points higher than that of tantalum, have low volatility and good stability at high temperatures.

It has been seen, however, that the contaminating material was removed at about 1,900° to 2,000° C. The only likely explanation for the removal of carbon or carbide was that it was oxidised by either the oxygen in the surface films on the original tantalum powder particles or in the residual gases in the vacuum system, or both. Earlier work<sup>3</sup> on the preparation of tantalum carbide has shown, however, that this reaction occurs at a much lower temperature (1,300° to 1,400° C.) than that at which the change described above takes place. For these reasons, together with the fact that it has not been possible to detect any carbon (or carbide) in the final sintered product by either microscopic or analytical means, it has been thought that the phenomenon was not due to carbon. It is well known that tantalum acts as a very powerful "getter," i.e., absorber of gases, and it is used extensively in electronic tubes, especially of the transmitting type, to remove permanently the residual gases in a tube after it has been sealed off. This work indicates that its most useful "gettering" temperature range is 1,600° to 1,900° C., these being the temperatures at which maximum increases in weight of the bar occur.

At temperatures of 2,000° C. and above another change occurred. The bar weight and the resistivity fell and the density increased at a much more rapid rate than at lower temperatures. Ideally, with pure metallic powders, the rate of sintering probably increases steadily with rise in temperature, but in actual practice it is generally the removal of hindrances to sintering rather than increased ductility (i.e., greater ionic mobility and, therefore, greater ease of movement of surfaces into contact) which is responsible for apparently sudden increases in sintering rate.

In this case, it was believed that at about 2,000° C. the impurities which had been absorbed at the lower temperatures, together with those which were there originally, began to be removed. However, instead of merely coming out of the tantalum in the same form as that in which they entered, it was believed that they were expelled as compounds of tantalum. If, for example, one of the impurities had been oxygen, then it was probable that tantalum oxide would be volatilised. This would explain the very large increase in weight loss compared with the earlier small gains. Whatever the reason for the changes in weight it was evident that temperatures below 2,000° C. would not be very satisfactory for sintering tantalum and that temperatures above 2,500° C. would be preferable. The final observation to be made from the results plotted in Fig. 1 was that the weight loss curve showed a point of inflexion at about 2,450° C. It was thought that the losses below this point represented for the most part those due to impurities and, at the point where they began to diminish, there came into operation another, more powerful, source of loss, namely, that due to volatilisation of tantalum metal. It will be noticed that the gradient

<sup>3</sup> Myers, R. H., and Greenwood, J. N., *Ibid.*, 1943, 129, 41.

of the upper part of the curve is steeper than that of the lower portion.

### Effect of Time

From observations made during the sintering of tantalum bars at high temperatures it was evident that longer times than 30 minutes would be required for the complete outgassing of the metal and, accordingly, a series of experiments was performed to determine the effect of time at 2,600° C. on the density and electrical resistivity. The temperature of 2,600° C. was chosen as being likely to be high enough to give satisfactory sintering in a reasonable time, while being not so high as to cause trouble from excessive loss of metal by volatilisation.

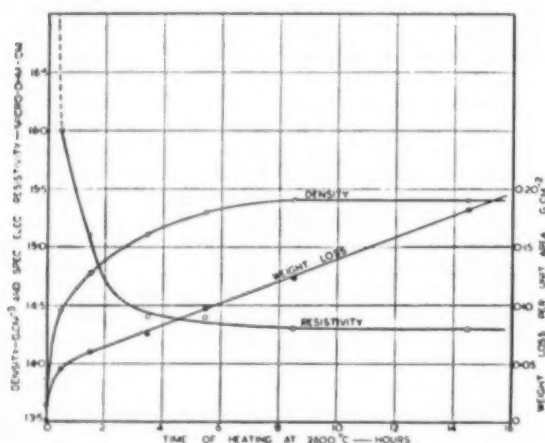


Fig. 3.—Curves showing the effect of time of heating in vacuo at 2,600° C. on density, specific electrical resistivity and weight loss of tantalum compacts.

The methods were as outlined in the previous section and the results are plotted in Fig. 3.

From the curves it will be seen that there was very little change in density or resistivity after about six hours' heating. Since the conductivity of a metal is particularly sensitive to impurities, either solid or gaseous, the flattening of the curve indicated that at least after six hours' sintering at 2,600° C. there was no further loss of impurities.

The loss in weight per unit area of radiating surface of a bar of tantalum heated *in vacuo* at 2,600° C. is plotted as a function of time in Fig. 3. After the initially high rate of loss the rate became constant and represented probably the loss due to evaporation of the metal. By calculation from the results obtained the rate of loss of metal due to evaporation at 2,600° C. was 9.4 mgm. cm.<sup>-2</sup> hour<sup>-1</sup>. This figure holds only for sintered bars where the real surface area would be appreciably greater than the apparent surface area due to the uneven surface.

### Power Required for Heating

In order to heat a bar 5 in. × ½ in. × ¼ in., the following conditions were needed:—

Temperature ° C.		Voltage per in. length of bar		Current— amps.
1,150	....	0.30	....	200
2,000	....	0.65	....	650
2,600	....	0.80	....	1,000

With longer bars the end losses due to the cooling effect of the grips would be relatively lower and consequently a somewhat lower power input than that calculated from these figures would be required to heat the bar to the same temperature.

### Conclusion

From a study of the curves given and from actual observations made during the heating of the tantalum bars it has been possible to lay down a sintering schedule for electrolytic tantalum powder which has yielded bars suitable for mechanical working. The main consideration was to pause in the heating when major changes occurred and Fig. 4 shows schematically the schedule adopted. The pause at 2,000° C. was to enable

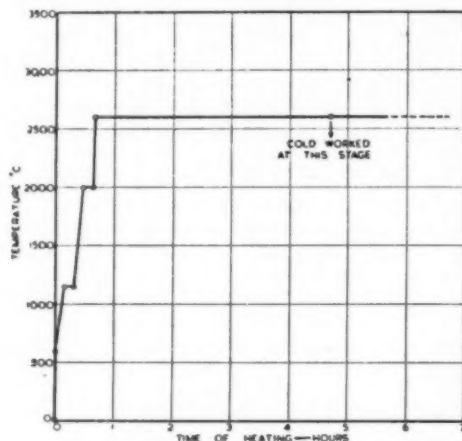


Fig. 4.—Sintering schedule adopted for tantalum bars.

the oxide and other impurities to be removed and the main sintering to proceed. The time at full temperature was shortened to four hours without any noticeable ill effect and, after a reduction in area of 40 to 60% by swaging, a further heat treatment at the same temperature for one to two hours was given. This achieved a closing up of the pores and still allowed a reasonable time for the metal to be thoroughly outgassed. The density at this stage was usually 16.5 to 16.6 g. cm.<sup>-3</sup>.

The hardness of the well sintered bars was 65 to 70 D.P.N. and during sintering they shrank about 4 to 5% in length. This shrinkage was considerably smaller than that occurring with metal powders such as tungsten or molybdenum.

### Acknowledgments

This work was financed from the Commonwealth Research Fund and was performed in the Baillieu Laboratory under the general direction of Professor J. Neill Greenwood whose counsel the author gratefully acknowledges.

### Squirrel Cage Rotors

HIGH DUTY ALLOYS LTD. are now in a position to manufacture rotors for squirrel cage electric motors with rotor bars and fan blades cast integrally in pure aluminium. Those interested in this new venture should send inquiries to High Duty Alloys Ltd., Slough, Bucks.

# Molten Salt Descaling by the Efco-Virgo Process

By J. A. Monks and J. McMullen, A.I.M.

*A descaling process is described, the main feature of which is the chemical and physical modification of the scale by the action of molten salts which are self-regenerative. Originally developed for descaling stainless steels, which do not readily respond to ordinary pickling methods, the process is being increasingly applied to both ferrous and non-ferrous alloys, especially with the more expensive alloys where the metal wastage in pickling is a serious item.*

THE descaling of steel in molten salts, now well established in America, is gradually assuming importance in this country as one of the major metallurgical developments of the post-war years. Designed originally for the stainless steels where the conventional acid pickle has never been really satisfactory, its immediate success has led to a much more general adaption so that while these steels still remain its principal field of application, the process is to-day being increasingly used for the whole range of carbon and alloy steels and more recently for some of the principal non-ferrous metals.

The criteria of any descaling operation depend, of course, to some extent on the material being treated. The time factor, always of importance, becomes of prime importance in the case of the stainless steels, and it is perhaps in this direction that the molten salt process has made its greatest contribution. At the same time, metal loss tolerated in the cheaper mild steels constitutes a serious debit item with the more expensive alloy steels while the danger of hydrogen embrittlement is a serious consequence when the descaling constitutes a finishing process especially on parts that are liable to stressed conditions in service. With the process to be described both these features are completely eliminated due to the use of a salt that is without positive action on the base metal and in which the chemical reactions concerned do not involve the presence of atomic hydrogen.

## The Nature of Scale

Although scale is basically a combination of the oxides of iron it is nevertheless true that the ease of removal in pickling varies widely both with the composition and thermal history of the steel. It is now generally agreed that the scale of plain carbon steels exists as three fairly distinct layers: An outer layer of ferric oxide, the higher oxide of iron; a middle layer of the magnetic oxide, often referred to as the magnetic phase, and the inner layer of a ferrous phase constituting the bulk of the scale. This latter is not true ferrous oxide as its oxygen content is somewhat greater than that demanded by the stoichiometric formula  $\text{FeO}$ . It can be more accurately described, at least at room temperatures, as a decomposition product of Wüstite, a solid solution of oxygen in ferrous oxide.

The proportion of the three phases present, as also their structure, are important in descaling, and it is known that they vary within fairly wide limits. Increase of temperature, for instance, in any given atmosphere, promotes the formation of Wüstite with a corresponding reduction in the amount of the other two phases, the

same occurring with decreasing oxidising effect of the furnace atmosphere.

In acid pickling it is largely the Wüstite which is attacked, probably by an electrolytic action made possible by the acid seeping through the cracks in the outer layers, and it is the dissolution of this phase that causes the outer layers to flake away. At the same time Wüstite is much more porous than the magnetic phase and is, therefore, of greater permeability to the acids, in fact, the action of the acid on the base metal itself, with the resulting bursting action of the hydrogen so formed, plays a big part in the actual pickling mechanism, being greater in the case of some acids like sulphuric than with others.

It is clear, therefore, that the amount and nature of the Wüstite phase is important as also is the nature of the outer layers. This is evidenced by the well-known difference in pickling behaviour between normalised and box-annealed sheet and the equally pronounced difference between rolled and annealed products. Any means, therefore, of modifying the scale, whether during or subsequent to annealing, would materially assist the pickling operation. It is also clear that the ideal pickling acid would be one that did not attack the base metal as metal loss and hydrogen embrittlement could then not occur. Although no such acid exists there is no doubt that some of the modern inhibited solutions do make some approach to this, with the result that pickling brittleness and metal wastage are minimised.

With the more highly alloyed steels, however, the scale is less simple as the oxides of some of the alloying elements, often of a highly refractory nature, are also present. In addition, the scale is generally continuous and tightly adherent so that there is more resistance to acid attack. Here, too, the thermal history of the steel has a marked effect.

The chromium steels are particularly notable in this respect, as one would surmise from their stainless and heat-resisting properties. In fact, with the higher chromium qualities the response to the usual stepped pickling process is so slow that really effective pickling on an economical basis is rarely attainable.

## The Efco-Virgo Process

The chief feature of this process is the chemical and physical modification of the scale by the action of molten salts at a temperature of  $480^{\circ}/540^{\circ}\text{C}$ . The scale so modified is then removed in the following two stages of the process which consist of a cold-water quench followed by, where necessary, a short immersion in warm dilute acid.



The salt used is of patented\* composition consisting of caustic soda, containing active ingredients which chemically convert the refractory oxide to one of a flocculent nature and capable of solution in a weak acid. This physical change is partly due to the volume increase of the scale which accompanies the chemical conversion and is such that the rupturing effect of the steam produced in the cold-water quench is sufficient to dislodge the greater part of it leaving the remainder as a loosely adherent fine deposit.

The finish thus produced is considered satisfactory in inter-process pickling where the deposit seems to act as a lubricant in the operations that follow. For bright work, however, the water quench is followed by a flash pickle in warm, dilute acid with a subsequent water wash. Alternatively, and depending upon the finish required the acid step may be in two stages—viz.:

- (a) 10% hydrochloric acid in water at 75°/80° C.
- (b) 10% nitric acid in water at 75°/80° C.

The duration of the acid dip is of the order of one minute, so that the possibility of diffusion of hydrogen into the base metal with resulting hydrogen embrittlement is avoided.

As the time of immersion in the molten salt varies from 2–20 minutes, depending upon the condition of the material, the total time cycle is of the order

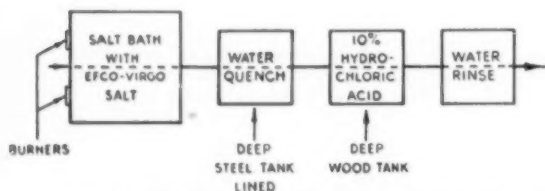


Fig. 1.—Efco-Virgo process, layout for batch descaling.

of 5–25 minutes, which for stainless steels represents a considerable reduction in time over that of older methods.

A unique feature of the salt is that it is self-regenerative—the activating agents in the salt, which convert the scale, being reconverted to their original composition by the action of atmospheric air. In heavily worked baths, however, it is sometimes necessary to accelerate the regeneration by blowing air through the salt at given intervals.

#### Plant Required

A schematic arrangement for the batch descaling of stainless steel is shown in Fig. 1, from which it will be seen that the plant required is relatively simple, and as the materials used are not excessively corrosive in nature the materials of construction call for little special care in selection.

The bath containing the caustic soda is of conventional design having a welded mild steel pot. The welding which is preferably done by the electric arc is important as it must ensure full penetration of sound weld metal at all corners. After welding the pot is stress-relieved by heating to 650° C. in a muffle furnace followed by cooling in still air.

\*U.S.A. Patent Re 22887 British Patent Application 13705/45.

The bath may be heated externally or internally although careful design is important for external heating to avoid flame impingement at the bottom. Should this occur any sludge build-up at that point would interfere seriously with heat transfer, with consequent risk of burning through. With internal heating this feature is absent, and as there is no thermal lag from pot to salt, maximum pot life is assured.

On a performance basis, the comparison is more pronounced, shorter time cycles being experienced in internally heated baths of the immersed electrode type. This reduction in descaling time is found to be more pronounced with increasing size of bath and is no doubt due to the circulatory motion of the salt caused by the electro-dynamic forces operating around the closely-spaced electrodes. Fig. 2 shows such a bath rated at 22-kWs. and embodying one pair of electrodes. With the larger capacity baths having correspondingly higher ratings, several pairs of electrodes are provided, each pair

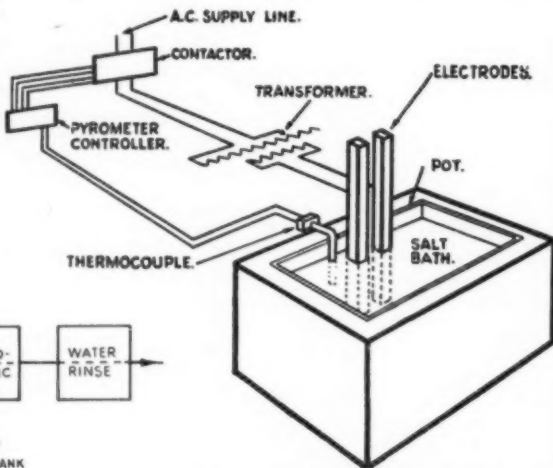


Fig. 2.—Diagrammatic illustration of Efco-Ajax-Hultgren salt bath with one pair of electrodes.

generating heat by virtue of the electrical resistance of the molten salt. In both cases the current is supplied at low voltage from a step-down transformer provided with tapings and an off-load tap changing switch to enable the input to be varied to suit the working conditions—i.e., starting up, normal working and stand-by.

#### Scope of the Process

Although first introduced for batch descaling of stainless steel components, continuous units are now in operation handling strip, wire and sheet for both inter-process and final descaling. Fig. 4 shows a typical arrangement for the descaling of continuous strip.

In the ferrous field the process shows its greatest advantage with the expensive alloy steels, where the metal wastage in pickling is a serious debit item and particularly in the stainless grades where in addition

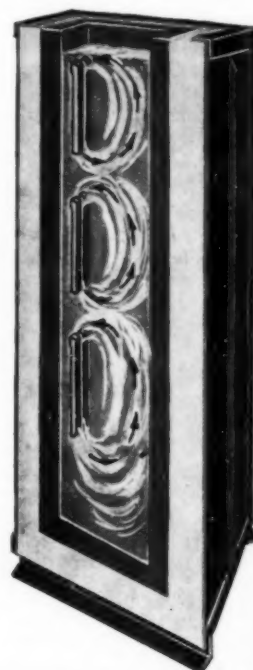


Fig. 3.—Efco-Ajax-Hultgren deep type salt bath showing electrodes cascaded.



efficient acid pickling is difficult and costly. In plain-carbon steels which are in general easily handled in acid-pickling plants, the advantages are less pronounced, nevertheless, large tonnage plants are in operation producing a superior finish with low running costs. The process is also being applied to the de-sanding of castings. The salt has found applications in isothermal treatment where according to the composition of the steel being treated, some measure of descaling can be effected at the quenching stage.

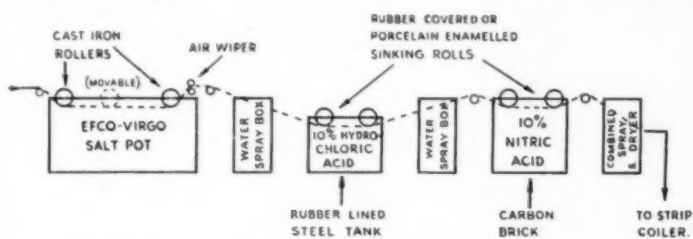


Fig. 4.—Efco-Virgo process—layout for continuous strip.

In the non-ferrous field nickels, coppers, high nickel-chromium alloys and some of the copper alloys, including the copper-silicon alloys are being successfully handled. In general, any alloy that is not attacked by caustic soda or whose properties are not impaired by heating to 500° C. can be descaled by this method.

The salt composition is the same irrespective of what alloy is being descaled, the temperature only being varied within the range quoted. The composition of the reagents used in the flash pickle may also vary with the alloy being treated.

#### Operating Features

Apart from the well-known precautions to be taken when handling caustic soda there are no particular features to be guarded against in operation. The plant, if large, should be adequately screened with hoist controls, etc., situated at the protective side of the screen.

As the bulk of the scale is removed in the water quench and only a little finds its way into the salt bath, frequent de-sludging is unnecessary. Experience is showing that weekly de-sludging is advisable in exceptional cases, but in the more general run, de-sludging at intervals of three to four weeks is all that is required.

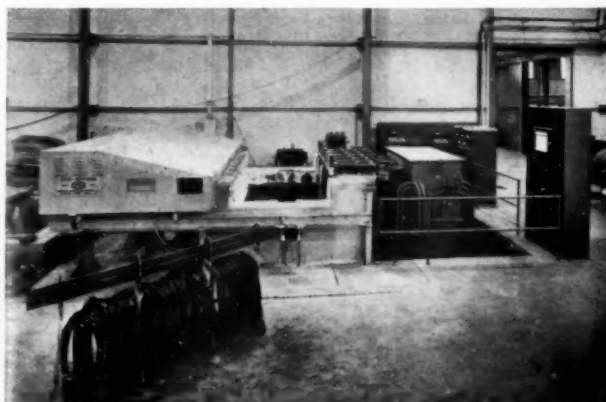


Fig. 5.—Installation for wire.

Make-up of the bath is governed entirely by drag-out as the self-regenerative nature of the salt is complete providing the ratio of surface area to depth is appropriate. With continuous and heavily-worked baths air blowing is sometimes necessary to accelerate the reactions. Salt consumption varies with the type of work being handled but is normally around 7-9 lb. per ton of work treated.

Coming now to the actual time cycle, this as would be expected, varies within fairly wide limits depending upon the steel, the nature and the weight of the scale.

Steel composition has a decided effect as seen by the difference in behaviour between the carbon manganese steels on the one hand and the nickel chromium constructional steels on the other, and again in the latter steels with and without molybdenum. Of much greater effect however, is the thermal history of the steel, whether, for instance, it is a high or low temperature scale that is to be removed, this latter point being well illustrated in the behaviour between hot-rolled and annealed austenitic steels, the difference being equally pronounced with varying furnace atmospheres.

It is found that such difference in susceptibility to salt attack can be taken care of by varying the bath temperature within the temperature range quoted, this method being much more effective than mere extensions of the descaling time. Providing a preliminary test sample is put through the bath to determine the best working conditions, there is normally no difficulty in working to the overall cycle time of 5-25 minutes.

The temperature and duration of the acid dip have been well established for the different steel qualities.

With the temperature of treatment fixed as above, the cycle of procedure is in general as follows:—

1. Ensure the load of steel to be descaled is dry.
2. Immerse in the salt bath for the required time at the required temperature.
3. Cold-water quench.
4. Acid dip No. 1.
5. Cold-water rinse.
6. Acid dip No. 2, if required.
7. Cold-water rinse.
8. If necessary to remove any adherent smut, hose off with a stream of water under pressure.



Fig. 6.—Installation showing Efco-Virgo salt bath with quench tank on the left.



Fig. 7.—Installation showing end of Efco-Virgo salt bath (right) with water quench tank and HCl tank on the left.

### The Advantages of the Process

The advantages of the process as found in actual practice may be summarised as follows:—

- i.—No need for preliminary degreasing operation, the salt itself having degreasing properties.
- ii.—Elimination of costly and time-consuming scale-breaking operations.
- iii.—No metal loss.
- iv.—Absence of hydrogen embrittlement.
- v.—A finish equal to, and in certain cases superior to that obtained in the conventional acid pickle.
- vi.—Pronounced shortening of the overall time cycle.
- vii.—Low running costs.
- viii.—Low cost of materials of construction.
- ix.—No replenishments other than that to compensate for drag-out.
- x.—No necessity for special control tests during working.
- xi.—Elimination of waste liquor disposal problem.

## Carbide Die Maintenance

By Richard Saxton

*Sintered carbide dies are now more generally used for cold-processing wire, bars and tubes, and considerable experience and technical knowledge are necessary to make and maintain these dies to ensure the production of uniformly satisfactory products. The production of these dies is referred to, and attention directed to, their maintenance in a serviceable condition.*

THE present widespread industrial application of sintered carbides is undoubtedly due to their continuous development since they were introduced in 1929; probably the most outstanding feature has been the supersession of the steel die as a cold-reduction unit for cold-processing wire, bars and tubes. Many of these dies have now attained the stage of being metallurgically and dimensionally standardised, and, although the field of development has been considerably narrowed, adaptation to further processes in industry is still increasing.

In the fabrication of dies for cold-reduction work, such as the production of wire or drawn bars, the basic processes involved are inherently simple, but they necessitate experience and technical knowledge to ensure the production of uniformly satisfactory products. The usual procedure is to mix carbide in finely powdered form with carbon, the object being to obtain a definite composition closely approaching a theoretical chemical compound. The mixture is then milled with a binder until each particle is coated with binder component. Further processing, prior to sintering, is to form the die nib, which is achieved by moulding the compound under pressure to furnish the approximate size and shape of nib; due allowance being made for shrinkage during sintering and to excess essential for finishing reduction section or hole to final dimensions.

Sintering is usually performed at atmospheric or under applied pressure. The die, as sintered, is generally of cylindrical formation, with a diameter slightly larger than height, particularly in diameters under 1 in. Compared with steel the sintered nib is hard and brittle, having a Rothwell C. hardness from 71—with 13% cobalt, to 82—with 3% cobalt, and a modulus of transverse rupture stress as high as 300,000 lb. per sq. in.

Sintered carbide, employed as a drawing or reduction die, retains its strength at elevated temperatures, a factor advantageous in the hot drawing of tungsten and molybdenum wires, two of the hardest metals to draw. Due to extreme brittleness under transverse pressure, the nib or reducing section necessitates encasing within a mechanically supporting member, and this backing, in general, is achieved by encasing the nib in steel. Various methods are employed to secure the casing, the chief of which are mechanical pressing, hot shrinking, and, with large dies, casting the casing around the nib.

The ideal assembly is probably one in which a spherical nib is set into a hollow spherical casing, in such a way that the compression forces of the casing would counterbalance the pressure exerted on the nib during the reduction of the material, but practical considerations, such as the necessity for holding the die in a definite position through plane or cylindrical surfaces, both during service and re-sizing, preclude the employment

of such a structure. A typical assembly is that shown by the cross-section in Fig. 1.

Although various views are held respecting the most efficient die contour, there is general agreement that the die-reduction zone should consist of a series of concentric

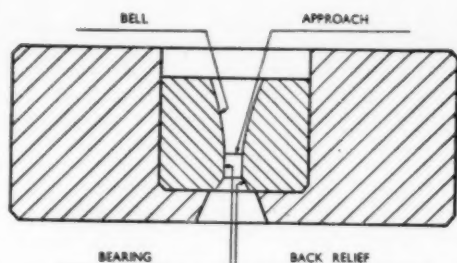


Fig. 1.—Illustrates a cross-section of a die enclosed in a metallic casing.

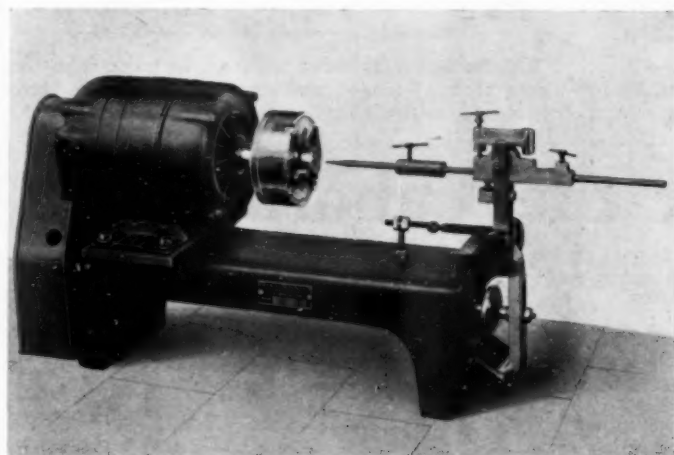


Fig. 3.—Illustrates a semi-auto die-polishing machine.

truncated cones, and a straight cylindrical bearing. For wire and bar production various angles are agreed as standard practice, but the influence of angle on die life is not too well known; the larger the angle with, incidentally, shorter reduction zone, the greater is the stress imposed. Experimental tests with various angles indicated that the larger the angle, with reduction confined to lesser area, greater friction and stress was imparted. In the case of the smaller angle, with work effect spread over a greater area of contact, production was higher and die wear lower.

Research work, conducted with a view of ascertaining power or pull of forces operating in reduction, reveals that as the material contacts in the reduction zone, it is reduced and elongated at a uniform rate, but the force generated is not constant; it increases as the reduction proceeds, due to increasing hardening of the material as deformation proceeds.

The part of the die subject to most wear is the approach-angle, in which a ring is formed unless corrected when wear is noted. Freedom from this defect is achieved by frequent polishing as and when the die is withdrawn from service. Polishing the approach-angle at frequent intervals minimises and almost eliminates wear of bearing, and considerable polishing may be performed without defection or alteration of die size. Where a ring is permitted to form, there is a tendency for edges to break off and cut out the die. Ring inclusions can usually be eliminated by employing a compound approach-angle—i.e., a 12° approach for a height of approximately

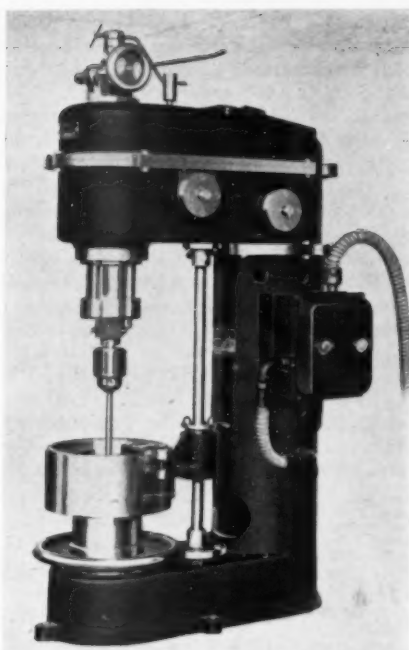


Fig. 2.—Illustrates type of machine employed for first processing or roughing-out.

$\frac{1}{16}$  in., followed by a 20°–22° angle for a further  $\frac{1}{16}$  in., and a 35° entering angle. Rings, in general, form at a line where the entering material contacts the approach-angle.

In the plastic deformation of high-carbon and hard alloy steels, which have a tendency to swell as they leave the die, it is good practice to use a 2°–3° lap when forming the bearing. This furnishes a back taper which prevents material drag in the travel of the bearing.

The removal of rings and opening of dies to a larger size, necessitates the employment of various grades of abrasives in conjunction with what is known as a "lapping" machine. In this process two types of abrasive are employed; first, boron-carbide in quality 240 grit; followed by No. 3 diamond powder dispersed in olive or castor oil. A type of machine used for first processing is shown in Fig. 2.

Boron-carbide as employed for removal of wear effects exerts a roughening action detrimental to material processing, and the application of No. 3 diamond powder is to eliminate scars or scratches formed by boron-carbide application. Following the No. 3 diamond powder the die is subjected to polishing. For final polishing, a machine such as is shown in Fig. 3 may be used, and abrasives employed are No. 4 or 5 grade diamond powder. A finer grade, No. 6 is obtainable, but is, in general, only employed to process dies of very small size, or where an exceptional fine polish is essential. Surface finish of wire, bar or tube is to a certain degree dependant on degree of polish imparted to the die, and the higher the polish less the frictional forces generated during the passage of the material through the reduction zone.

The practice of purchasing abrasives in dry powder form and dispersing in olive or castor oil is resultant in



waste and variation in cutting properties, leading to variation in polishing speeds. To offset loss by waste and inefficient application two new forms of abrasive application have been introduced. The first are tools called "metal-bonded quills," and consist of small steel lengths with a surface impregnation of diamond dust. Cylindrical types are produced for fabricating or polishing the cylindrical orifice known as the bearing, and also tools with conical ends. These latter are fabricated with a 30°-60° included angle, and have proved highly efficient in grinding out the approach-angle.

The second form is what is termed an "applicator" gun, and is used for the application of a measured amount of diamond-oil compound during die processing. This tool, which is similar to a hypodermic syringe, is designed to extrude exactly metered amounts, eliminating guess work and waste. With the gun a cartridge is supplied, in which the graded compound is sealed. Various grades of grinding compound are obtainable in this form, each distinguishable by an identifying colour,

clearly visible through the cartridge glass and opening in the gun barrel. For fine work, where the compound must be applied in minute amounts, a reduction needle is available. This attaches to the nozzle of the gun, and dispenses the compound in pin-point quantities.

Although diamond abrasives are a more expensive agent than the boron or silicon carbide qualities, their superior cutting properties, with resultant saving in time, far outweighs the extra cost. Their hardness in comparison with various carbides and hardened steel is as follows:—

Hardened Steel	.. .. .	500
Tungsten Carbide	.. .. .	1,500
Silicon	.. .. .	2,000
Boron	.. .. .	2,200
Diamond	.. .. .	8,250

This indicates diamond hardness as more than four times that of silicon carbide, and three and three-quarter times the boron.

## Costing for the Laboratory

By Laurence J. A. Haywood

Chief Chemist, Catton & Co., Ltd., Yorkshire Steel Foundry, Leeds

*An account is given of a system of costing applied to the work of a foundry chemical laboratory in order to apportion the costs against the appropriate section of the works rather than against the main production department as a whole.*

**C**OSTING of laboratory operations appears to have received less detailed attention than for other departments of the works, and whereas the majority of costs can be calculated with the maximum of accuracy, those for the laboratory are frequently debited wholly against the main production department with no attempt at apportionment to the appropriate sections of the works.

To some extent, doubtless, this system has been aided and abetted by the commonly accepted statement that operational costs play a relatively minor part as compared with salaries, which represent the largest item. This is, of course, a dangerous philosophy, since it implies that incidental expenses cannot, or need not, be controlled, whereas the reverse is in fact the case. And just as every section of the works should have its share of laboratory services, so should these departments bear their relative share of operational costs.

The writer has given considerable attention to this question during the past few years, and would suggest that the systems to be described represent at least a sound working basis. In practice they have been adopted by the foundry, the laboratories of which the writer has the honour to control, where they have proved eminently satisfactory, and whilst they refer in the main to metallurgical and allied analysis (within which field the writer has had the greatest experience), the principles are nevertheless applicable with only slight modification to all types of laboratory work and any branch of industry.

Whilst it may be stated here that no claim is made to absolute originality, the writer has not seen any comparative system described in print, nor does he know of any works

where the principles described are applied exactly as discussed and to the extent and detail recommended herein.

### Costing System Requirements

Essentials for operation of the system are:—

1. Accurate stock records with prices,
2. Accurate daily totals of routine estimations carried out,
3. Itemised costs for each stage of routine analytical procedure,

This involves a further point—viz.:—

4. Standardised procedure for estimation of each element, and arising from the fact that certain types of work such, for example, as slag and refractory analysis cannot be standardised in this way (owing to the complexity of the chemical operations involved and the consequent necessity to treat each sample individually):
5. Different methods of costing must be used for routine and "special" work.

It is proposed to discuss these points in turn, with illustrations of the writer's methods, which have proved

AMMONIUM PERSULPHATE									
NEW STOCK					ISSUES		BALANCE		
Ordered	Rec'd	Quantity	Unit	Value	Date	Quantity	Date	Quantity	Value
				£ s d		lb oz		lb oz	£ s d
26-11-46	10-12	7	lb oz	12 3					
12-3-47	20-3	7	1 9	12 3					
	Stock Check				4-47	4	4-47	10	17 6
2-6-47	9-6	14	1 9	1 4 6					
	Stock Check				8-47	15	8-47	9	15 9
30-9-47	7-10	14	1 9	1 4 6					
	Stock Check				12-47	12	12-47	11	19 3
2-2-48	9-2	14	1 9	1 4 6					
	Stock Check				4-48	10	4-48	15	1 6 5

Fig. 1.—Stock record card.



DATE 7-6-48 ANALYST									
ELEMENT C									
Sample	Spec.	Sample	Spec.	Sample	Spec.	Sample	Spec.	Sample	Spec.
100	2	100	2	100	2	100	2	100	2
4354		4632		4834		5100		5371	
81-2852		4354		4632		4834		5100	
1102		268		202		276		271	
RL-86610									
392									
Result	-39	-26	-19	-265	-26				
100	2	100	2	100	2	100	2	100	2
3074		2414		2857		3080		3152	
81-1674		2074		2414		2857		3080	
400		240		443		223		272	
RL-86610									
390									
Result	-39	-33	-435	-215	-26				
100	3	100	11						
5671		5671							
81-5371									
400									
Result	-39								
100	3	100	11						
3572									
81-3152		3572							
450									
Result	-41								

Fig. 2.—Gravimetric work recorded on special form.

most satisfactory in operation, of arriving at the information required.

### Stock

Stock consumption is recorded on the cards illustrated in Fig. 1. This will be seen to present a complete history of the item, indicating not only the amount consumed during any period and the amount currently in store, but also the value thereof. This considerably simplifies the assessment of cost per estimation, and also enables a rapid check to be made of the total value of goods in store, for general stock-taking purposes. In addition, the listing of dates of ordering and receipt shows the time-lag in delivery, giving a self-indicating system as to when re-ordering becomes necessary without either overstocking or complete exhaustion.

The cards, conveniently in different colours for chemicals and glassware, are brought up-to-date monthly in conjunction with the writer's established principle of monthly ordering of equipment. Stock may be checked at convenient intervals—Fig. 1 shows intervals of four months—the figures being arrived at from the totals of estimations carried out. In the smaller laboratories, of course, it may be simpler to assess actual stocks than to compute consumption from analyses; this is a matter for individual decision, but it should be pointed out that assessment from actual work done, with occasional check against actual stock, will indicate leakages or wasteful usage not necessarily found by stock checks only.

DATE 7-6-48 ANALYST									
ELEMENT C - P									
Sample	Spec.	Cell	Rdg.	Chart	Result	Sample	Spec.	Cell	Rdg.
1	100	2	57		40	1	100	2	40
2	100	2	57		34	2	100	11	38
3	100	11	57		34	3	100	1	32
4	100	1	59		32	4	100	5	34
5	100	5	60		31	5	100	2	39
6	100	2	60		31	6	100	1	39
7	100	1	59		32	7	100	2	34
8	100	3	53		38	8	100	3	32
9	100	2	49		42	9	100	3	35
10	100	3	49		42	10	100	2	32
11	100	2	52		38	11	100	11	34
12	100	11	59		32	12	100	1	36
13	100	1	57		34	13	100	?	56
14						14	100	?	39
15						15	100	?	39
16						16	100	?	39
17						17	100	?	45
18						18	100	?	45
19						19			
20						20			

Fig. 3.—"Spekker" work recorded on special form.

The second item may be easy or difficult of assessment; difficult if no proper system of recording the work is in vogue, easy if this is done in orderly and logical fashion. Figs. 2 and 3 show forms drawn up by the writer, the first for use in connection with gravimetric or titrimetric work, the second for use with the "Spekker." These are illustrated in actual use, Fig. 2 showing carbon in steel analyses, and Fig. 3 showing silicon and phosphorus, determined absorptometrically by one operator who runs the two methods side by side. From these sheets, which are collected daily and retained for reference as required, the daily totals of estimations are easily deduced and tabulated as shown in Fig. 4. It will be noticed that standardisations are listed separately from actual estimations, for reasons which will become obvious in due course.

### Chemical Costs

Item 3 is simply arrived at by setting out in detail the method of analysis to be used for each estimation, and calculating from stock record cards the cost of each addition. A typical example, given in Table I, shows costs (as fixed in the writer's laboratory) for the "Spekker" determination of manganese in steel.

Item 4 can quickly be dealt with. It is almost universal practice nowadays for all analytical procedures

DATE	STANDARDS					STEELS										TOTALS
	C	Si	Mn	S	P	C	Si	Mn	S	P	Ni	Cr	Mo	V	W	Co
June 7	4	2	6			24	24	24	22	22	2	2	2	-	-	-
8	4	2	7			21	22	23	26	26	-	6	-	2	-	-
9	4	3	6			25	26	27	22	22	3	5	3	1	2	-
10																
11																
12																
13																
14																
15																
16																

Fig. 4.—Daily work record.

to be standardised for any one laboratory, and where differences exist between individual analysts they are normally so slight as to be negligible. There may, of course, be more than one "standard" procedure for each element, but a simple differential designation will cover that. Again, however, this point leads directly to item 5.

In all cases where any form of standardised procedure or routine cannot be adopted, the alternative system of costing, to be dealt with later, must be used. At this stage we are concerned with routine processes only.

### Glassware

Having established the chemical cost of each estimation, we have now to take into account the important item of glassware. Since all beakers and flasks broken in carrying out the work are as irredeemably lost as the chemicals destroyed in the reactions, they must be debited against those estimations if the cost figure is to represent the truth. We refer again, therefore, to our stock record cards to find the consumption of glassware. It should be noted here that as far as possible different types or sizes of beaker or flask should be used for different estimations, but where this is impracticable it will be found reasonably accurate to apportion breakages in direct ratio to the totals of estimations carried out, as deduced from the record in Fig. 4. From these figures the average cost of estimations in terms of glassware can be obtained, and added to the chemical cost. In the writer's laboratory it is necessary to add 0.25d. to the total shown in Table I, so that the cost of one manganese estimation becomes 1.22d., and in order to give an easily workable figure (and to provide a slight tolerance for chemical wastage) this is approximated to 1.25d.

TABLE I

	Cost in Pence
20 mls. "Spekker" Acid .. .. .	0.40
1 ml. Nitric Acid 8.6, 1-12 .. .. .	0.03
10 mls. Silver Nitrate 2.5% .. .. .	0.39
10 mls. Ammonium Persulphate 25% .. .. .	0.12
10 mls. Urea 5% .. .. .	0.03
	0.97

Estimations such as carbon and sulphur in steel, involving the use of combustion tube furnaces, are less straightforward. In addition to the cost of chemicals and glassware it is necessary to take into account the life of the combustion tubes and furnace windings or other type of element. It is, however, not a difficult matter to record replacements and if these are averaged over a given period in the same way as glassware breakages, a remarkably accurate figure will be obtained of the addition to be made per estimation for these items. Details for sulphur determination in the writer's laboratories are given in Table II.

TABLE II

	Cost in Pence
1 Combustion Boat .. .. .	1.54
10 mls. Hydrochloric Acid 50% .. .. .	0.05
Starch .. .. .	0.01
Titration solutions .. .. .	negligible
	1.60
Add cost of tubes, furnace elements and sundry breakages	1.35
	2.95

For ease of working, this figure is approximated to 3.0 pence per estimation.

Variations in quality of boats and tubes are not found in practice seriously to affect the calculated costs, provided a reasonable period, say one year, is used as a basis. Furnace elements may have a variable life, but a fair average is not difficult to assess.

### Standard Analyses

The question of standard analyses must next be considered. In certain cases, notably the combustion sulphur determination, they are an integral part of the process and without them results are unobtainable. Added to the normal cost of the estimation must be the cost of the standard steel used. Where this is an internally-prepared sample it can, as a rule, be ignored. Where, however, such steels as British Chemical Standards are used, their cost must be included, giving an extra charge for standard determinations. This charge is averaged against the number of estimations carried out, to give the ultimate cost per estimation. For example, it was found over a period that 1,109 sulphur standards were carried out in order to enable 6,475 steels to be reported. As internally-prepared standards were in use, the estimation cost remained the same—viz., 3.0d. Therefore, in the ratio of one standard to six steels, the ultimate cost of one sulphur estimation becomes 3.5d.

From this point the normal costing procedure is followed. In the Laboratory Day Book is entered the Works Departmental Number from which the sample originated. The total of estimations carried out weekly for each department is obtained, together with the cost. These costs are expressed as percentages of the total analysis costs for the week, and from these figures the cost department can make the necessary allocations of expenditure.

### The "Pound-Hour" Basis

Turning next to the question of analyses which can not be standardised, the simplest system of dealing with these appears to be on a "pound-hour" basis, arrived at in much the same way as the familiar "man-hour" of industry. If the total weekly salaries of all members of the lab. staff be multiplied by the number of working hours, a "pound-hour" figure will be obtained. The individual salary of each operative will correspond to his particular code and the hours worked by him on any one job will be his "pound-hours" total for that job. By collating these figures and transcribing to percentages, the proportion of the gross cost of the laboratory to be allocated to the various departments can readily be arrived at.

By way of example, suppose a small laboratory to have two junior and three senior analysts, whose rates of remuneration are: A and B, £3 weekly; C, £6 weekly; D, £7 10s. weekly; and E, £9 weekly. The total "pound-hours" is thus 28.5 times the number of hours worked per week, in this case 40, giving a base figure of 1,140. The individual code figures are, respectively, 3, 6, 7.5, and 9.

Each analyst returns a weekly work-sheet similar to that shown in Fig. 5, from which information the cost department can compute the proportionate allocation as already described.

In the example quoted, the system may be simplified to the extent that the salary figures are in the ratio 1 : 2 : 2.5 : 3, giving a smaller number for calculation. But as they may be expected not to remain in that proportion permanently, any modification needs careful thought beforehand.

It may be preferred to work to the nearest day or half-day in these calculations, as providing sufficient accuracy. This may serve admirably where all working days are of the same duration or where the mid-day break splits

# WORK RECORD SHEET

Analyst _____		W.E. 11 June 1948					
Dept. No.	Project No.	Mon	Tues	Wed	Thur	Fri	TOTAL
12		4	4	3	5	4	20
14		1	1	1	-	1	4
17		-	2	-	1	-	3
	1101	2	-	-	-	-	2
	1103	1	-	2	1	2	6
	1104	-	1	2	1	1	5
TOTAL							40

Fig. 5.—Work record sheet.

the period into two equal parts, but where a morning session, for example, is of 4½ hours and the afternoon only 3 hours, difficulties may arise. However, this is a question which can conveniently be solved for each individual works laboratory. Whatever details are adopted, the essence of the system remains unaltered.

## Special Apparatus

Two further items are left for consideration. The first is the question of special apparatus needed for an investigation. Where this will serve for one particular purpose only, it must obviously be debited against the job for which it was acquired; if it will serve for a number of functions in current use, the cost will naturally be split in rough proportion. This does not, of course, refer to any large item of capital expenditure which would normally be treated separately.

It might also be well to consider whether the equipment is suitable or available for disposal after use, since this would bring in a credit return to offset expenditure incurred in the investigation.

The second item is the cost of chemicals used in

analysis. It frequently happens that this is so small as to be relatively negligible; otherwise two courses of action are open—viz., either to endeavour to list separately all items consumed and compute their cost (which may ultimately develop into an undertaking of its own!) or, simpler and preferred, to apportion the cost in relation to the hours worked, which will probably be found sufficiently accurate for all practical purposes.

So far we have dealt with routine standard work and non-standard work separately, but it usually happens that both types of work are carried out simultaneously by the same staff. This need present no extra difficulty, since the weekly work sheet shown in Fig. 5 is capable of providing all the required information. It will, however, be necessary to check stock records of all chemicals used in routine work from actual numbers of such estimations carried out, and assume that the difference between the figure so arrived at and the actual physical stock is accounted for by "special" work. This amount will be noted carefully over a given period and reduced to terms of cost per week, to be taken into account as described in the section dealing with non-standard work only. Although necessarily an approximation, it will nevertheless be found more accurate than mere guesswork, and certainly better than not making any attempt whatever to apportion costs in their correct sphere.

## Acknowledgments

Acknowledgments are due to Mr. Alfred H. Catton, Managing Director, Messrs. Catton & Co., Ltd., Yorkshire Steel Foundry, Leeds, for permission to publish this work, and the author is grateful to his colleague, Mr. N. M. Patterson, for valuable comment and assistance.

## Recommended Practice for Spot Welding Mild Steel\*

FOR the first time in this country it has been possible to put forward recommendations giving the absolute value of each of the main welding variables required for producing optimum results in spot welding mild steel sheet. The recommendations are based almost entirely upon actual experimental results obtained by investigators of the British Welding Research Association during the past three years.

In the past, it has been customary to set spot welding machines for a given job on a purely arbitrary basis and pay little attention to absolute value of the machine variables. This practice makes it difficult to transfer established settings from one machine to another, and in any case machine setting can be a most time-consuming operation. Owing to the absence of suitable instruments for setting absolute values of the welding variables, these difficulties have been accentuated, but now that suitable instruments have become available, due largely to the efforts of the Association's FR.5 Committee on Development of Devices for Measuring Current, Pressure and Time in Resistance Welding, there are no valid reasons why instrumentation cannot be adopted.

The scope of the recommendations are such as to cover thickness of low carbon mild steel sheet ranging

from 20 S.W.G. to 14 S.W.G. inclusive. Additional tests are to be undertaken shortly so that the recommendations will ultimately cover a wider range of thickness, viz., 24 S.W.G. to ½ in. inclusive. In addition to the information on optimum machine settings, the recommendations put forward actual dimensions of the spot welds obtained and values are given of the order of strength to be expected from spot welded joints. The question of permissible edge distances is discussed, data are given upon the settings required for spot welding multiple and different thicknesses, and reference is made to the effect of using one electrode of a normal truncated cone shape, with the other electrode of the pad type to preserve surface finish and avoid indentation.

The main recommendation for the optimum values of welding variables, weld strength, weld size, edge distance and pitch are summarised in a single table. Further tables show the effect of changes in each of the variables on weld strength, the increase in secondary current required to maintain weld size at various weld pitches and the effect of edge distance on the failing load of single spot welds. The final table gives the maximum range of values of welding current and welding time in which the recommended conditions are maintained. The value of this lies in the fact that it is not always possible to set welding current exactly to a required value, but the difference could be compensated by an appropriate adjustment in welding time.

\* The complete Report is published in the October, 1948, issue of the Welding Research Supplement to the Transactions of the Institute of Welding.



# The Resistance of Alloys to Corrosion During the Processing of Some Foods\*

By J. F. Mason, Jr.†

*Comparatively few quantitative tests have been published on the relative corrosion resistance of metals and their suitability for particular foodstuffs. Especially is this so in the case of alloys. The present paper is an exception, since it reports the results of investigations on a large number of metals and alloys in operating equipment under actual service conditions and gives direct comparisons of the relative performance of the various materials studied.*

IT is the purpose of this paper to present the results of a number of miscellaneous plant and laboratory corrosion tests in the handling and processing of foodstuffs which have not already been published by The International Nickel Company. The corrosion resistance of materials for pea, corn and tomato processing and the resistance of pure nickel, and Inconel to corrosion by milk are discussed in detail elsewhere.<sup>1</sup> Additional data on the corrosion resistance of metals in the production of, and the effect of metals on, wines, distilled liquors and beers have also been published.<sup>2</sup>

The durability of equipment is only one part of the corrosion problem in food processing plants. Of at least equal importance are the possible effects of corrosion products on the quality of the products. In this connection, it has been found that nickel equipment, as it is used in food processing, is non-toxic. This statement is based on the results of several investigations made to determine the safety of using nickel equipment in the preparation of foods. An excellent summary of the situation was made by Drinker, Fairhall, Ray and Drinker<sup>3</sup> of the Department of Physiology, Harvard School of Public Health who supplemented a study of the work of other investigators by tests of their own.

Similar research by Titus, Elkins, Finn, Fairhall and Drinker<sup>4</sup> has established also that the chromium-nickel-iron alloys (stainless steels) are fully acceptable from the hygienic standpoint for food preparation utensils.

It was further demonstrated by the work of Pratt<sup>5</sup> at the University of Rochester that nickel does not catalyze the destruction of vitamins in milk, one of the most perishable of foods. He compared in his studies milk containing on the average about fifteen parts per million of nickel with milk containing no nickel and his principal conclusion was that nickel dissolved from a nickel vessel did not destroy or catalyze the destruction of vitamins A, B, or C during the pasteurisation process.

Additional investigations by Ziels and Schmidt<sup>6</sup> have also established that nickel is superior to most, if not all, other metals with respect to the absence of catalytic effects on the development of rancidity in fats and oils during steam deodorisation which is one of the most

critical steps in the quality processing of edible oils and shortenings.

In addition to corrosion resistance and effect of metals on the product, another factor that should be taken into consideration in the selection of materials for food-processing equipment is heat transfer. A large percentage of food processing operations involves heating or cooling something. Consequently, the materials used to hold the product and separate it from the heating or cooling media should not interfere too much with the transfer of heat. It is, of course, true, but not always recognised, that the resistance to heat-flow offered by a metal wall is only one of several resistances which include, of greatest importance, films of the substance being heated, or of the heating medium which cling to the metal wall. Furthermore, there may be solid films of corrosion product, scale or baked-on substances which increase the resistance to heat-flow.

Where the sum of all the resistances to heatflow is high, that of the metal may be of insignificant importance, and the choice of metal will not have much effect on the overall rate.

In the food-processing industry about the only equipment where the total resistance to heat-flow is low enough to make that of the metal itself appreciable are steam-jacketed kettles and certain high-velocity heat-exchange apparatus, such as multi-tubular heaters and coolers. With tubular apparatus the gauge of the metal tubes is relatively thin, so that the maximum difference between the materials of highest conductivity, silver and copper, and those of low conductivity, stainless steel and Inconel, is rarely more than about 10% and often negligible. This is also true of heating coils.

In the case of steam-jacketed kettles, the gauge of metal is often fairly thick— $\frac{1}{2}$  in. or more—and since the overall rate of heat transfer is high—more than 400 B.T.U./sq. ft./° F./hour—the effect of the metal itself may be appreciable. In a particular case it was found that water could be boiled in a copper kettle in six minutes, in a nickel kettle in seven minutes, whereas an Inconel or stainless-steel kettle required twelve minutes.

Comparatively few quantitative tests have been published on the relative corrosion resistance of metals and their suitability for particular foodstuffs. Especially is this so in the case of alloys. Comparison with other possible metals has rarely been made, and lack of standardisation of testing conditions renders comparison difficult. In our field investigations, use was made of the spool-type specimen holder which permitted the simultaneous testing of a large number of metals and alloys in operating equipment under the actual conditions of service, thus giving direct comparisons of the relative performance of the various materials studied.

\* Presented at the recent Convention of the National Association of Corrosion Engineers in the United States of America.

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1 Inco technical bulletins T-28 and T-26.

2 Bulletin TS-6 (International Nickel Company, Inc.).

3 "The Hygienic Significance of Nickel." *The Journal of Industrial Hygiene*, Vol. VI, No. 8, pp. 307-356, December, 1924.

4 "Contamination of Food Cooked or Stored in Contact with Nickel-Chromium-Iron Alloys." *The Journal of Industrial Hygiene*, Vol. XII, No. 8, pp. 306-313, October, 1930.

5 "Does the Nickel Dissolved from the Container During Pasteurisation Catalyze the Destruction of the Vitamins of Milk?" *Journal of Nutrition*, Vol. 3, No. 2, pp. 141-55, 1930.

6 "Catalytic Effect of Metals and Light on Fats and Oils." *Oil and Soap, Journal of the American Oil Chemists' Society*, Vol. 22, No. 12, pp. 327-330, December, 1945.



The method of test was substantially in accord with A.S.T.M. Recommended Practice for Conducting Plant Corrosion Tests, A224-41.<sup>7</sup> Briefly, the assembly consisted of previously cleaned and weighed specimens of the several metals and alloys to be tested, mounted on the spool-type holder with non-metallic parts of bakelite or porcelain to separate and insulate the specimens from each other and from the metallic parts of the holder. Two similar specimens of each material were included on each spool. The completed test assemblies were fastened firmly in place in the desired test locations in operating plant equipment and allowed to remain for sufficient lengths of time to give reliable indications of corrosion behaviour. In some instances, also, the duration of the several exposures was determined by the cycle of processing operations which included cleaning of the test pieces as the equipment was cleaned and sterilised in the ordinary way. Each of the test specimens used had an exposed area of 0.5 sq. dm.

7 A.S.T.M. Standards, Part I, p. 523, 1944.

Upon completion of tests, the spools were removed, dismantled and the specimens examined, cleaned of all scale and corrosion product, and reweighed. From the weight losses, areas of specimens and duration of exposure, the corrosion rates were calculated in terms of milligrams per square decimeter per day (mdd), and these rates transposed to inch penetration per year (ipy), the unit used in the accompanying tables. This unit is based upon the assumption of uniform corrosion in practice from one side of the metal only. The rate shown for each material is the average of the two specimens included in each test. In addition, each specimen was examined for cracking, pitting, and other forms of local attack. Where pitting or local attack occurred, depth of the five or ten deepest pits was measured microscopically or with a depth gauge. In the accompanying tables maximum depth of pitting is reported, where it occurred.

Nominal compositions of the metals and alloys included in one or more of these tests are shown in Table I.

TABLE I.—NOMINAL COMPOSITIONS OF METALS AND ALLOYS USED IN CORROSION TESTS

Material	Nickel %	Copper %	Chromium %	Iron %	Molybdenum %	Silicon %	Manganese %	Carbon %	Other %
Monel .. .. .	67.0	30.0	—	1.4	—	0.1	1.0	0.15	—
Nickel .. .. .	99.4	0.1	—	0.15	—	0.05	0.2	0.1	—
Inconel .. .. .	78.5	0.2	14.0	6.5	—	0.25	0.25	0.08	—
18-8 SS (Type 302) .. .. .	8-10	—	17-19	Bal.	—	0.75 max.	2.0 max.	0.20 max.	—
18-8 SS (Type 304) .. .. .	8-10	—	18-20	Bal.	—	0.75 max.	2.0 max.	0.08 max.	—
18-8 SS (Type 347) .. .. .	9-12	—	17-19	Bal.	—	1.0 max.	2.0 max.	0.08 max.	—
18-8 SS (Type 316) .. .. .	10-14	—	16-18	Bal.	2-3	1.0 max.	2.0 max.	0.10 max.	—
14-18% Cr Steel (Type 420) .. .. .	—	—	14-18	Bal.	—	1.0 max.	1.0	0.12 max.	—
10-14% Cr Steel (Type 410) .. .. .	—	—	10-14	Bal.	—	0.75 max.	0.60 max.	0.15 max.	—
Copper .. .. .	—	99.9	—	—	—	—	—	—	—
Silicon Bronze .. .. .	—	96.0	—	—	—	3.0	1.0	—	—
Chemical Lead .. .. .	—	—	—	—	—	—	—	—	Pb 99.9
Hastelloy B .. .. .	60.0	—	—	6.0	32.0	1.0	1.0	—	—
Hastelloy C .. .. .	51.0	—	17.0	6.0	19.0	1.0	1.0	—	—
Durimet T .. .. .	22.0	1.0	19.0	Bal.	3.0	—	—	0.07 max.	—
Duriron .. .. .	—	—	—	Bal.	—	14.5	—	—	—
Tin .. .. .	—	—	—	—	—	—	—	—	—
Zinc .. .. .	—	—	—	—	—	—	—	—	—
Mild Steel .. .. .	—	—	—	Bal.	—	—	0.3-0.5	0.20 max.	—
Ni-Resist (Type 1) .. .. .	13.5-17.5	5.5-7.5	1.75-2.50	Bal.	—	1.0-2.5	1.0-1.5	3.0 max.	—
Cast Iron .. .. .	—	—	—	Bal.	—	1.5-2.5	0.5-1.0	3.0-3.5	—

TABLE II.—PLANT AND LABORATORY CORROSION TESTS IN FRUIT JUICES AND SYRUPS

Material	Condition	Corrosion Rate Inch Penetration Per Year			
		Inconel	Nickel	Monel	18-8
Tomato Juice .. .. .	Aerated, Room Temperature .. .. .	0.0000	0.012	0.003	—
Tomato Juice .. .. .	Un-aerated, Room Temperature .. .. .	0.0000	0.008	0.0001	—
Tomato Juice .. .. .	*Fully Aerated, 170° F. .. .. .	0.0002	0.044	0.015	0.0003
Tomato Juice .. .. .	*Fully Aerated, 195° F. .. .. .	0.0002	0.016	0.008	0.0002
Lemon Juice .. .. .	Aerated, Room Temperature .. .. .	0.0003	0.020	0.010	—
Lemon Juice .. .. .	Boiling Under Reflux .. .. .	—	0.014	0.0006	—
Lemon Juice .. .. .	Un-aerated, Room Temperature .. .. .	0.0003	0.0005	0.0005	—
Lemon Syrup .. .. .	Fully Aerated, Room Temperature .. .. .	0.0000	0.001	—	0.0000
Lemon Syrup, Diluted .. .. .	Fully Aerated, Room Temperature .. .. .	0.0002	0.034	—	0.0004
Lime Syrup, Acidified into Citric Acid .. .. .	Un-aerated, Room Temperature .. .. .	0.0002	0.0001	0.0001	0.0001
Pineapple Juice .. .. .	Aerated, Room Temperature .. .. .	0.0000	0.013	0.005	—
Pineapple Juice .. .. .	Un-aerated, Room Temperature .. .. .	0.0000	0.004	0.0007	—
Pineapple Juice .. .. .	*Alternate Immersion, 152°-178° F. .. .. .	0.0004	0.010	0.006	0.0001
Pineapple Juice .. .. .	*Fully Aerated, 180° F. .. .. .	0.0007	0.036	0.030	0.0002
Pineapple Juice .. .. .	*165°-175° F., 16-18 in. Vacuum .. .. .	<0.0001	0.0045	0.003	0.0003
Grape Juice .. .. .	Aerated, Room Temperature .. .. .	0.0000	0.025	0.005	—
Grape Juice .. .. .	Un-aerated, Room Temperature .. .. .	0.0000	0.006	0.002	—
Grape Juice .. .. .	*Boiling Under Reflux .. .. .	0.0004	0.007	0.0003	0.0001
Orange Juice .. .. .	Boiling Under Reflux .. .. .	0.0000	0.0007	0.0007	—
Orange Syrup .. .. .	Fully Aerated, Room Temperature .. .. .	0.0002	0.025	—	0.0000
Orange Syrup, Diluted .. .. .	Aerated, Room Temperature .. .. .	<0.0001	0.0004	0.0005	—
Apple Juice .. .. .	Un-aerated, Room Temperature .. .. .	0.0000	0.0001	0.0001	—
Apple Juice .. .. .	*Un-aerated, Room Temperature .. .. .	<0.0001	0.001	0.0009	0.0001
Apple Cider .. .. .	Un-aerated, Boiling .. .. .	<0.0001	0.002	0.0012	<0.0001
Grapefruit Juice .. .. .	3-7% Citric Acid, Hot .. .. .	0.0002	0.0002	0.0001	0.0002
Grapefruit Juice .. .. .	2-7% Citric Acid, Cold .. .. .	0.0006	0.0006	0.0005	0.0007
85% Grapefruit Juice & 15% Orange Juice .. .. .	*Aerated, Room Temperature .. .. .	<0.0001	0.022	0.002	<0.0001
Caramel Colour Syrups .. .. .	*Un-aerated, 212° F. .. .. .	0.0014	0.0015	0.0011	<0.0001†

\* Indicates field tests.

† Specimens pitted to a max. depth of 0.001 in. on surface and 0.011 in. in crevice formed by bakelite and metal surface.

## Fruit Juices and Syrups

Table II gives the results of a number of plant and laboratory corrosion tests on Monel, nickel, Inconel and 18-8 stainless steel in a variety of fruit juices and syrups under different conditions of exposure. Generally, it will be noted that the materials tested performed satisfactorily, and this is borne out in practice since they are used rather widely for equipment in the processing, storage and dispensing of fruit products. However, in some applications where the corrosive conditions are especially severe due to a combination of high temperature and strong aeration, Inconel and 18-8 stainless steel prove to be the better materials. Furthermore, when requirements are such that virtually complete freedom from tarnishing of equipment is desirable, Inconel and 18-8 stainless steel are preferred. Generally, tarnishing neither injures the product nor materially decreases the life of the metal, but it may be objectionable on the basis of appearance when the fabricated apparatus is installed where it may be viewed by the public. In spite of occasionally higher rates of corrosion and susceptibility to tarnishing, pure nickel is more widely used than any of the other materials for steam-jacketed cooking kettles where economic advantage is derived from its high rate of heat transfer.

## Pectin

This product is a complex carbohydrate present in certain fruits and its extraction and handling present certain corrosion problems with the more common materials of construction due to the addition of hydrochloric or sulphurous acids during processing. It will be noted from the field-test data given in Table III that the greatest amount of corrosion occurred in the case of Test 5, where the specimens were exposed to the pectin

liquor acidified with hydrochloric acid during evaporation. These data do not show any significant superiority of Inconel over the 18-8 types of stainless steel, but experience has indicated the former to be the preferred alloy for pectin evaporators. The austenitic stainless steels are known to have a susceptibility toward local attack in the form of pitting in contact with hot, dilute solutions of hydrochloric acid and, for this reason, rather than any incidence of pitting in the relatively short corrosion tests, they are not considered as reliable for the application in question. The use of Monel in this service has been limited by the desire to exclude possible sources of copper contamination, even though it possesses a usefully low corrosion rate.

There do not seem to be any particular corrosion difficulties in handling the pectin liquor during degassing, collecting and storage since most of the materials exhibited very low rates of attack. However, in the treating tank where carbon is used for clarification there is a good chance for galvanic corrosion to take place between carbon particles and the metal wall to which they may adhere. This effect has been observed by the author in other similar services where carbon was employed for purification, but in the present case no such phenomenon was noted, probably due to the relatively short duration of test.

## Glutamic Acid and Monosodium Glutamate

Glutamic acid is one of the amino acids generally obtained from the hydrolysis of protein-containing materials such as Steffens Filtrate, occurring in the process of making sucrose from sugar beets, and wheat gluten. It is used along with other amino acids principally as a source of food for quickly rehabilitating undernourished people and for the production of monosodium glutamate which is employed as a condiment in the flavouring of meats and other foodstuffs.

The plant test data shown in Table IV are representative of the corrosive conditions encountered in various

TABLE III.—PLANT CORROSION TESTS IN THE PROCESSING OF FRUIT PECTIN

TEST 1.	In degassing tank containing thin pectin liquor at a pH of 2.7-4.0-2% malleic acid and 0.065% $SO_2$ . Average temperature, 120° F. Duration of test 30 days. Some aeration and agitation.
TEST 2.	In carbon-treating tank containing thin pectin liquor at a pH of 3.8-4.0-26% malleic acid and 0.3% carbon. Temperature, 95°-150° F. Duration of test 4 days, during which 6 treatments were carried out, each requiring 15 hours. Agitated constantly with air.
TEST 3.	In collecting tank containing thin pectin liquor at a pH of 3.8-4.0-26% malleic acid. Average temperature, 135° F. Duration of test 3 days, during which 6 batches were collected, each requiring 11 hours. No aeration and slight agitation.
TEST 4.	In storage tank containing thin pectin liquor at a pH of 2.95-4.0-26% malleic acid and 0.05% free $SO_2$ . Average temperature, 80° F. Duration of test 26 days, during which tank was drained every 24 hours and fresh liquor added. No aeration, but some agitation due to emptying and filling tank.
TEST 5.	In evaporator handling pectin liquor acidified with HCl to a pH of from 2.4-2.1. Temperature, 105° and 140° F. under vacuum of 28 in. Hg. The evaporation was completed in two stages—the first at 105° F. for 9 hours and the second at 140° F. for 8 hours. Duration of test, 52 hours, including the 17-hour boiling period. No aeration, but agitation due to ebullition.
TEST 6.	In storage tank containing concentrated pectin liquor at a pH of 3.30-4.1% malleic acid and traces of sulphites. Average temperature, 100° F. Duration of test, 27 days. No aeration, but slight agitation due to dropping of liquor from the evaporator to the storage tank.

Material	Corrosion Rate, Inch Penetration Per Year					
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
Monel .. .. .	0.006	0.0013	0.0009	<0.0001	0.0011	0.0006
Nickel .. .. .	0.023	0.0025	0.0015	0.0029a	—	0.0012
Inconel .. .. .	0.0001	<0.0001	0.0001	<0.0001	0.0003	<0.0001
18-8 SS (Type 302) .. .. .	<0.0001	<0.0001	0.0001	<0.0001	—	<0.0001
18-8 SS (Type 304) .. .. .	<0.0001	<0.0001	0.0001	<0.0001	0.0006	<0.0001
18-8 Mo SS (Type 316) .. .. .	<0.0001	<0.0001	*0.0001	<0.0001	0.0005	<0.0001
18-8 Cu SS (Type 347) .. .. .	0.0002	—	—	<0.0001	0.0004	<0.0001
Copper .. .. .	0.009	0.0018	0.0012	0.0001	—	0.0018
Silicon Bronze .. .. .	0.009	0.0026	0.0014	0.0001	—	0.0023

a Local attack in the form of pitting to a maximum depth of 0.007 in.

TABLE IV.—PLANT CORROSION TESTS IN THE PROCESSING OF GLUTAMIC ACID AND MONO-SODIUM GLUTAMATE

TEST 1.	In flash chamber of evaporator concentrating crude glutamic acid at a pH of 5.6 from 1.25 specific gravity to 1.33 specific gravity. Average temperature, 158° F. No aeration but considerable vapour velocity entering at rate of 720 fpm. Duration of test, 36 days.
TEST 2.	In a crystalliser handling glutamic acid in a saturated solution of sodium chloride at a pH of 3.2. Average temperature, 77° F. Duration of test, 28 days. Continuously aerated and agitated by air.
TEST 3.	In a crystalliser handling mono-sodium glutamate in a saturated solution of sodium chloride at a pH of 5.0-6.4. Average temperature, 86° F. Duration of test, 28 days. Continuously aerated and agitated by air.

Material	Corrosion Rate Inch Penetration Per Year		
	Test 1	Test 2	Test 3
Monel .. .. .	0.0036	0.0026	0.0015
Nickel .. .. .	0.0064	0.0033	0.0017
Inconel .. .. .	<0.0001	0.0034	<0.0001
18-8 SS (Type 302) .. .. .	0.0001d	0.0018a	0.0002c
18-8 SS (Type 304) .. .. .	0.0002e	0.0021a	0.0014e
18-8 Mo SS (Type 316) .. .. .	<0.0001	0.0011	<0.0001c
13% Cr Steel (Type 410) .. .. .	0.0073f	0.0032g	0.0007c
Hastelloy B .. .. .	—	0.0019	0.0007
Hastelloy C .. .. .	—	—	—
Durimet T .. .. .	—	—	—
Duriron .. .. .	—	—	—
Durichlor .. .. .	—	—	—
Mild Steel .. .. .	0.022	0.007	0.011
Ni-Resist .. .. .	0.008	0.004	0.003
Cast Iron .. .. .	0.017	0.006	0.020

a Specimens perforated during test. Original thickness .. .. . 0.031 in.

b Local attack in the form of pitting to a max. depth of .. .. . 0.006 in.

c .. .. . 0.004 in.

d .. .. . 0.002 in.

e .. .. . 0.007 in.

f .. .. . 0.015 in.

g .. .. . 0.012 in.

steps in the production of these chemical compounds. The figures indicate that in these services a number of the materials tested were subject to local attack in the form of pitting and in several cases to the extent of perforation. Both Monel and Inconel exhibit satisfactorily low corrosion rates in the evaporator and crystallisers and these data are in harmony with, and have been confirmed by practical experience with, the use of these materials for such equipment.

## Gelatin

Mineral acids, principally hydrochloric acid, are used in the extraction of gelatin from animal tissues (bones, ligaments and skin). The results of a number of plant corrosion tests in the production and storage of gelatin involving the presence of hydrochloric acid are given in Table V. The figures indicate that Monel, nickel and Inconel, as well as the austenitic stainless steels and the straight chromium varieties, are highly resistant to corrosion, but because of the susceptibility of the latter materials to local attack, they are not generally used. On the other hand, since Monel and nickel are not subject to this type of attack, they are used rather extensively for such equipment as evaporators, drying nets, heating coils, kettles, storage tanks, etc. Inconel has been found to provide exceptional resistance to the destructive corrosive and mechanical forces encountered by gelatin drying nets and has become the preferred material for this service.

TABLE V.—PLANT CORROSION TESTS IN THE PRODUCTION OF GELATIN

- TEST 1.**—In the evaporation of gelatin solution at a pH of 3.8-6.8 from 4-20% solids. It was reported that traces of sulphuric, hydrochloric and nitric acids as well as sulphur dioxide were present in the gelatin solution. Temperature, 172° F. Duration of test, 27 days. No aeration, but agitation due to ebullition.
- TEST 2.**—In the storage of gelatin solution with hydrogen peroxide under alternate acid and alkaline conditions. Temperature not reported but presumed to be atmospheric. Duration of test, 30 days. No aeration or agitation.
- TEST 3.**—In 15-30% gelatin solution during extraction from animal hides by cooking in dilute hydrochloric acid. Average temperature, 180° F. Duration of test, 24 days. Slight aeration and mild agitation.
- TEST 4.**—In 0-10% gelatin solution during extraction from pig skins by cooking in dilute hydrochloric acid. pH of gelatin solution, 4-0. Temperature varied from 115°-212° F. Duration of test, 43 days. Slight aeration and agitation.
- TEST 5.**—In 0-10% gelatin solution during extraction from ossein (animal bone marrow) by cooking in dilute hydrochloric acid. Temperature varied from 135°-212° F. Duration of test, 43 days. Slight aeration and agitation.

Material	Corrosion Rate, Inch Penetration Per Year				
	Test 1	Test 2	Test 3	Test 4	Test 5
Monel	—	0-0004	0-0044	—	—
Nickel	0-0019	0-0007	0-0042	0-0008	0-0017
Inconel	<0-0001	<0-0001	<0-0001b	<0-0001	<0-0001
18-8 SS (Type 302)	<0-0001	0-0002	<0-0001	<0-0001	<0-0001
18-8 SS (Type 304)	<0-0001	0-0001	<0-0001	<0-0001	<0-0001
18-8 Mo SS (Type 316)	<0-0001	<0-0001	—	—	—
17% Cr Steel (Type 430)	0-00010a	—	0-0003c	<0-0001	<0-0001
13% Cr Steel (Type 410)	—	—	—	0-0004d	0-0008e

- |   |   |    |    |    |    |    |    |    |    |    |           |
|---|---|----|----|----|----|----|----|----|----|----|-----------|
| a | Local attack in the form of pitting to a max. depth of . . . . . 0.006 in.  |    |    |    |    |    |    |    |    |    |           |
| b | Local attack in the form of pitting to a max. depth of 0.003 in. on one specimen and 0.014 in. on other specimen. |    |    |    |    |    |    |    |    |    |           |
| c | Local attack in the form of pitting to a max. depth of . . . . . 0.004 in.  |    |    |    |    |    |    |    |    |    |           |
| d | 55  | 57 | 58 | 59 | 60 | 55 | 56 | 57 | 58 | 59 | 0.005 in. |
| e | 55  | 56 | 57 | 58 | 59 | 60 | 55 | 56 | 57 | 58 | 0.008 in. |

### Mayonnaise and Salad Dressing

From the data presented in Test 1 and 2 in Table VI, Inconel, 18-8 stainless steel and the 17% chromium steel are the most suitable materials for whips and beater bowls in contact with mayonnaise at atmospheric temperature since all are immune to significant attack and, as found from careful examination, free from tarnish. Nickel and Monel are less suitable chiefly because of their tendency to tarnish, which may or may not be considered a serious objection. The manufacture

TABLE VI.—LABORATORY AND PLANT CORROSION TESTS IN MAYONNAISE AND OTHER SALAD DRESSINGS

- TEST 1.—In mayonnaise beater bowl containing mixed spices, sugar, salt, eggs, salad oil and vinegar. Temperature atmospheric. Duration of test 5 days. Mixture was both aerated and agitated.
- TEST 2.—In storage of the above mayonnaise. Temperature atmospheric. Duration of test, 21 days. No aeration or agitation.
- TEST 3.—In boiling solution of 1% by weight acetic acid (as vinegar) and 5% salt used in the preparation of salad dressing. Temperature boiling. Duration of test, 160 hours and 20 days. No aeration but agitation due to ebullition.
- TEST 4.—In the above salad dressing after cooking. Temperature atmospheric. Duration of test, 21 days. No aeration or agitation.

Material	Corrosion Rate, Inch Penetration Per Year			
	Test 1	Test 2	Test 3	Test 4
Monel .. .. .	0-006	<0-0001	0-029	<0-0001
Nickel .. .. .	0-017	<0-0001	0-025	<0-0001
Inconel .. .. .	—	<0-0001	0-020	<0-0001
18-8 SS (Type 302) ..	—	<0-0001	0-002a	<0-0001
18-8 SS (Type 304) ..	0-0003	<0-0001	0-002a	<0-0001
18-8 Mo SS (Type 316) ..	—	—	—	—
17% Cr Steel (Type 314) ..	0-0003	—	—	—

a Local resting with several deep pits.

of cooked salad dressing requires the use of materials for the cooking kettles that can withstand the effects of prolonged contact with boiling solutions of vinegar and salt, and it is evident from Test 3 that such mixtures are very corrosive. None of the materials tested showed up satisfactorily, since Monel, nickel and Inconel exhibit rather high rates of corrosion and the 18-8 stainless steels, while they possess low rates of attack, as measured by weight loss, were subject to rather severe local attack.

Experience has demonstrated, however, that 18-8 molybdenum stainless steel (Type 316) represents the best choice of material for handling such mixtures. Even so, this stainless steel shows some tendency towards pitting, which can be kept to a minimum by having the surface of the steel as highly polished as possible and by cleaning the surfaces to remove any salty solids after each use.

There is another trick that has been used with good results in the manufacture of salad dressing, and that is to delay the addition of salt to the product as long as possible, that is, to add all the other ingredients first and then when the product is just about finished, add the salt. This, of course, reduces the time during which the material must resist attack by the acetic acid-salt mixture.

### Coffee Brew and Extract

The results of Test 1, tabulated in Table VII, represent the average of seven different determinations of the weight loss sustained by the samples of each metal. It is evident from these data that beverage coffee has only a very slight action on all the metals and alloys included in the test. Similarly, the corrosive effect of coffee extract, as shown by the results of Test 2, is also

TABLE VII.—LABORATORY AND PLANT CORROSION TESTS IN COFFEE BREW AND EXTRACT

- TEST 1.—In beverage coffee made by circulating 2 gallons of water through 1 lb. of ground well-known brand coffee contained in a clean muslin bag. Temperature, 195°–200° F. Duration of test, 2 hours. No aeration, but agitation due to flow of water.
- TEST 2.—In coffee extract contained in a stone crock. Temperature, 40° F. Duration of test, 30 days. No aeration or agitation.

Material	Corrosion Rate Inch Penetration Per Year	
	Test 1	Test 2
Monel .. .. .	0-0007	0-0001
Nickel .. .. .	0-0027	0-0003
Inconel .. .. .	0-0015	0-0001
18-8 SS (Type 304) .. .. .	0-0010	0-0001
Tin .. .. .	0-0060	—



negligible in nature. The wide use and satisfactory performance of Monel and 18-8 stainless for coffee-making equipment bear out the results of these findings.

### Vanilla Extract

A field test was made during the maceration and percolation of vanilla beans in an alcoholic solvent in the production of concentrated vanilla extract and the results are given in Table VIII. The service conditions did not prove to be at all severe and all the materials tested gave negligibly low corrosion rates. Incidentally, as a result of this test, the user selected Inconel for his processing equipment not only because of its very low corrosion rate, but also on account of the fact that it retained its original appearance to a much greater extent than the other materials tested.

TABLE VIII.—PLANT CORROSION TEST IN THE PRODUCTION OF CONCENTRATED VANILLA EXTRACT

CONDITIONS OF TEST.—Specimens exposed to alcoholic solvent and vanilla beans during steeping and percolation. Average temperature, 68° F. Duration of test, 162 days. Aeration, none, but some agitation due to periodic circulation.

Material	Corrosion Rate Inch Penetration Per Year
Monel .. .. .	0-0007
Nickel .. .. .	0-0008
Inconel .. .. .	<0-0001
18-8 SS (Type 302) .. .. .	<0-0001
18-8 SS (Type 304) .. .. .	<0-0001

### Carbonated Water and Beverages

These fluids while they are not especially corrosive as shown by the test results given in Table IX are highly sensitive to off-flavour due to the pickup of small amounts of certain metallic salts, notably copper and iron. In the past, block tin was used almost exclusively in this service, but in recent years due to the shortage of this metal, more and more items of equipment such as carbonators, dispensing machines and lines have been fabricated of nickel, Inconel and the austenitic stainless. These materials have performed very satisfactorily from the corrosion-resistance standpoint and, like tin, do not contribute any detectable metallic contamination to the beverages. Monel has found relatively limited application because of its copper content. A new type of nickel tubing has been developed which is essentially carbon free and possesses a very high degree of ductility and ease of coiling. This property has led to its wide use as a replacement for tin for cooling coils and leader lines from carbonators to dispensers.

The preferred materials for handling the carbonated fruit syrups in addition to tin are Inconel and the 18-8 stainless steels.

TABLE IX.—LABORATORY CORROSION TESTS IN CARBONATED WATER AND BEVERAGES

TEST 1.—In carbonated water under CO<sub>2</sub> pressure of 50-lb. gauge. Temperature, atmospheric. Duration of test, 5 days. No aeration or agitation.  
TEST 2.—In carbonated lime flavoured water under CO<sub>2</sub> pressure of 40-lb. gauge. Temperature atmospheric. Duration of test, 5 days. No aeration or agitation.  
TEST 3.—In carbonated ginger ale containing 0-03% citric acid. Temperature atmospheric. Duration of test, 32 days. No aeration or agitation.

Material	Corrosion Rate Inch Penetration Per Year		
	Test 1	Test 2	Test 3
Monel .. .. .	0-0001	0-0002	<0-0001
Nickel .. .. .	0-0001	0-0002	<0-0001
Inconel .. .. .	0-0001	0-0001	—
18-8 SS (Type 302) .. .. .	<0-0001	0-0001	—
18-8 SS (Type 304) .. .. .	<0-0001	0-0001	—
Block Tin .. .. .	<0-0001	0-0006	0-0006

### Meat Juice Extract

The production of meat juice extract by evaporation does not seem to be a significantly corrosive service as shown by the rather low rates of attack suffered by the materials tested in Table X. Monel and nickel are generally the preferred materials for use in contact with solutions containing small amounts of hydrochloric acid which are either added purposely to processing liquors, or are formed by hydrolysis in the reaction. The stainless steels are generally considered less reliable because of susceptibility to local attack in the presence of hydrochloric acid.

TABLE X.—PLANT CORROSION TEST IN THE VACUUM EVAPORATION OF MEAT JUICE EXTRACT

CONDITIONS OF TEST.—Animal tissue containing 0-5-40% organic solids and inorganic salts of sodium and potassium chlorides as well as about 3% phosphates. Hydrochloric acid used for acidification to a pH of 4-0-5-0. Temperature varied from 120°-180° F. Duration of test, 60 days, during which evaporator operated only 120-5 hours. No aeration, but some agitation due to evaporation.

Material	Corrosion Rate, Inch Penetration Per Year	
	Based on 60 Days Total Exposure	Based on 120-5 Hours Actual Evaporating Time
Monel .. .. .	0-0003	0-0033
Nickel .. .. .	0-0010	0-011
Inconel .. .. .	<0-0001	0-0002
18-8 SS (Type 302) .. .. .	<0-0001	0-0002
18-8 SS (Type 304) .. .. .	<0-0001	0-0002
Mild Steel .. .. .	0-0055	0-061
Ni-Resist .. .. .	0-0004	0-0045
Cast Iron .. .. .	0-0045	0-050

### Vinegar

The results of plant corrosion tests in the storage of vinegar and in its handling during pasteurisation are given in Table XI. The data indicate that the materials studied under the particular conditions of the test were all highly resistant to corrosion. An increase in the corrosion rates of Monel and nickel may be observed in the case of the test at 140° F., but they are still of a sufficiently low order to make the use of these materials practical. Inconel and the austenitic stainless steels were in no way affected by the change in temperature, and these alloys have proved to be highly useful for handling vinegar solutions of all concentrations up to boiling, both aerated and unaerated. Some materials like Monel, nickel and copper are strongly affected by aeration in the presence of such solutions and under the

TABLE XI.—PLANT CORROSION TESTS IN THE HANDLING OF VINEGARS

TEST 1.—In vinegar storage tank containing concentrations up to 100 grain. One set of specimens was exposed near bottom of tank and another set near liquid level. Temperature atmospheric. Duration of test, 240 days. No aeration at bottom of tank, but alternate exposure to air at liquid level when tank was emptied and filled. No agitation except on emptying and filling tank.  
TEST 2.—In vinegar pasteuriser, at times containing both grain and cider vinegar. Temperature, 140° F. Duration of test, 220 days. No aeration or agitation.

Material	Corrosion Rate Inch Penetration Per Year		
	Test 1		Test 2
	Near Bottom of Tank	Near Liquid Level	
Monel .. .. .	0-0002	0-0002	0-0014
Nickel .. .. .	0-0003	0-0005	0-0019
Inconel .. .. .	<0-0001	<0-0001	<0-0001
18-8 SS (Type 302) .. .. .	<0-0001	<0-0001	<0-0001
18-8 SS (Type 304) .. .. .	<0-0001	<0-0001	<0-0001
Tin .. .. .	0-0022	0-0004	—
Copper .. .. .	—	—	0-0036

TABLE XII.—PLANT CORROSION TESTS IN PICKLING AND CANNING BRINES

- TEST 1.—In tank containing herring and pickling brine consisting of 13% sucrose, 2% acetic acid, plus small amount of salt from herring and balance water. Temperature, 40° F. to atmospheric. Duration of test, 116 days. No aeration or agitation.
- TEST 2.—In olive brine tank containing sodium chloride and small amount of lactic acid. Temperature, cold. Duration of test, 220 days. No aeration or agitation.
- TEST 3.—In cucumber pickle preheater containing cider and grain vinegar plus sugar. Temperature, 140° F. Duration of test, 85 days. No aeration or agitation.
- TEST 4.—In kettle used in the preparation of onion pickling brine consisting of 3% sodium chloride, 2% acetic acid and 35% sugar. Temperature, boiling. Duration of test, 2 hours. No aeration, but agitation due to ebullition.
- TEST 5.—In vessel containing sausage casing brine consisting of sodium chloride plus sulphate and sulphur compounds. Temperature atmospheric. Duration of test 4 days. No aeration or agitation.
- TEST 6.—In sauerkraut brine containing vinegar and sodium chloride. Temperature atmospheric. Duration of test, 120 days. No aeration or agitation.
- TEST 7.—In pea brine tank containing a mixture of 10 lb. salt and 25 lb. sugar in 100 gallons of water. Temperature, boiling. Duration of test, 10 individual tests were made lasting from 8-10 hours each, and the data are based on an average of the maximum and minimum rates observed. No aeration or agitation.
- TEST 8.—In corn brine tank containing a mixture of 20 lb. salt and 100 lb. sugar in 100 gallons of water. Temperature, boiling. Duration of test—5 individual tests were made lasting from 8-10 hours each, and the data are based on an average of the maximum and minimum rates observed. No aeration or agitation.

Material	Corrosion Rate, Inch Penetration Per Year							
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
Monel .. .. .	0-0001	0-0019	—	0-0008	0-0008	0-0001	0-0010	0-0018
Nickel .. .. .	0-0001	0-0023	0-0035	0-0031	0-0007	0-0005	0-0011	0-0010
Inconel .. .. .	△0-0001	△0-0001	△0-0001	△0-0001	0-0002	△0-0001a	—	—
18-8 SS (Type 302) .. .. .	△0-0001	△0-0001	△0-0001	△0-0001	0-0001	△0-0001	—	—
18-8 SS (Type 304) .. .. .	△0-0001	△0-0001	△0-0001	△0-0001	—	—	0-0006b	0-0003b
18-8 Mo SS (Type 316) .. .. .	△0-0001	—	—	—	—	—	—	—
Copper .. .. .	—	0-0033	—	0-015	—	—	0-024	0-027
Tin .. .. .	—	—	—	0-030	—	—	0-005	0-0056
Mild Steel .. .. .	0-0004	—	—	0-11	—	—	—	—
Zinc .. .. .	—	—	—	—	—	—	0-030	0-040

a Local attack in the form of pitting to a maximum depth of 0-008 in.

b Specimens showed small rust spots.

circumstances they generally do not prove satisfactory where more than slight corrosion cannot be tolerated.

### Pickling and Canning Brines

These solutions are generally made up with small amounts of organic acids, such as acetic or lactic, plus salt and/or sugar. Table XII gives the results of eight plant corrosion tests in pickling brines for herring, olives, cucumbers, onions, sauerkraut and sausage and in canning brines for corn and peas. No significant amount of corrosion occurred on the majority of the materials tested, but a few of them showed pitting corrosion or incipient local attack as evidenced by the formation of rust spots. Copper, tin, mild steel and zinc were not generally satisfactory and, in fact, exhibited a relatively low order of corrosion resistance. Monel, nickel and Inconel have all proved by practical application to be well suited for handling these various brines and they are usually preferred along with Type 316 stainless steel for equipment used in this service. Types 302 and 304 stainless steel have, on occasion, shown a definite susceptibility to local attack resulting in

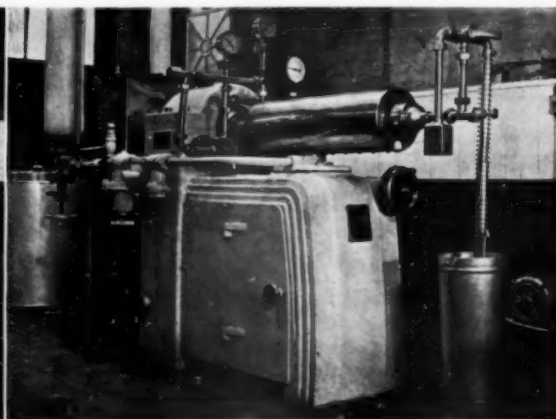
premature failure in contact with these brines, and must be considered of questionable suitability for this sort of service.

### Manufacture and Washing of Sausage Casing

The results of two corrosion tests made in a glycerinising tank used in the manufacture of cellulose sausage casing, and in the washing of sausage casing after extrusion, are given in Table XIII. The materials investigated in Test 1 exhibited a rather strong tendency towards localised attack with the exception of Type 316 stainless steel. This material remained free of pitting and proved to have a negligibly low overall corrosion rate as measured by weight loss. Test 2 was much less severe insofar as pitting was concerned and indicated the suitability of Monel, nickel and Type 304 stainless steel for this type of service. Under this exposure condition Inconel was again subject to local attack and, while Type 316 stainless steel was not included in this study, it would, undoubtedly, have performed at least as well as the Type 304 stainless steel.



A line of 8-steam-jacketed Monel lined pans made by A. Johnson Ltd., Park Royal, and installed in the works of Edward Manwaring Ltd., Peckham Hill Street, London, S.E.15, for processing malt vinegar (5% acetic acid).



Nickel freezer tubes on this Vogt instant freezer made by Cherry-Burrell Ltd., Chiswick, London, W.4. These machines are claimed to be responsible for the major part of the world's production of high quality ice cream.

TABLE XIII.—PLANT CORROSION TESTS IN THE MANUFACTURE AND WASHING OF SAUSAGE CASING

TEST 1.—In glycerizing tank containing 10% glycerine solution, adjusted to pH 6.0 with acetic acid, and purified cellulose sausage casing strip. Average temperature, 140° F. Duration of test, 61 days. Slight aeration and agitation.

TEST 2.—In washing of sausage casings after extrusion. Wash water contained 0.4% sulphuric acid and 1.25% sodium sulphate. Temperature, 104° F. Duration of test, 60 days. Slight aeration and agitation due to continuous circulation of the water.

Material	Corrosion Rate Inch Penetration Per Year	
	Test 1	Test 2
Monel .. .. .	0-0049a	0-0067
Nickel .. .. .	0-0058b	0-0071
Inconel .. .. .	0-0041c	0-0048c
Type 304 SS .. .. .	0-0004c	0-0037
Type 316 SS .. .. .	0-0001	—

a Local attack in the form of pitting to a maximum depth of 0-003 in.  
b Local attack in the form of pitting to a maximum depth of 0-015 in.  
c Specimens perforated during test. Original thickness, 0-031 in.

### Oleomargarine

The data given in Table XIV were obtained from plant corrosion tests in the production and handling of oleomargarine. It is evident that in the boil-down tank only cast iron is subject to rather high rates of attack, while the other materials tested are adequately resistant to corrosion. Copper or copper salts are known to have a strong influence in developing rancidity in fatty acids and for this reason the material is generally not considered satisfactory for use in such service. While Monel contains about 30% copper, its corrosion rate is usually of such a low enough order that it has been employed successfully for handling such acids.

Unfortunately, in connection with Test 2, Monel and nickel were the only materials investigated and, under the conditions, they demonstrated usefully low rates of corrosion, with nickel showing a superiority of better than 9 to 1.

TABLE XIV.—PLANT CORROSION TESTS IN THE PRODUCTION AND HANDLING OF OLEOMARGARINE

TEST 1.—In boil down tank in the production of oleomargarine from animal fatty acids. Eleven batches of oleomargarine were boiled from 10-20 minutes each and left to settle over night. The acid water used was about 0-75% strength. Temperature varied from atmospheric to boiling. Duration of test, 38 days, during which 160,000 lb. of stock were worked. No aeration, but agitation due to boiling.

TEST 2.—In the transportation of oleomargarine made from a mixture of beef fat and buttermilk with a calculated acid content of 0-35%. Temperature atmospheric. Duration of test, 1 day. No aeration or agitation.

Material	Corrosion Rate Inch Penetration Per Year	
	Test 1	Test 2
Monel .. .. .	0-0012	0-0019
Nickel .. .. .	0-0012	0-0002
Inconel .. .. .	0-0009	—
18-8 SS (Type 302) .. .. .	0-0001	—
18-8 SS (Type 304) .. .. .	0-0001	—
Copper .. .. .	0-0040	—
Ni-Resist .. .. .	0-0042	—
Cast Iron .. .. .	0-0020	—

### Tartaric Acid

In the production of cream of tartar, wine lees are treated with sulphuric acid and other chemicals to release the tartaric acid which is subsequently concentrated by evaporation and crystallisation. The results of a plant corrosion test in a vacuum pan evaporator concentrating pure tartaric acid to 57% are given in Table XV. It will be noted that both copper and lead suffered relatively high rates of corrosion as compared to Monel, nickel and Inconel. Prior to the running of this test, both copper and lead were the materials most generally used for

tartaric acid evaporators and they did not prove to be altogether satisfactory. On the basis of the superior performance shown by Monel in the test, it was specified for some evaporating equipment and practical experience has demonstrated that it was a wise choice of material. Monel is giving a much longer service life than ever obtained with either copper or lead and currently it is being used rather widely for various types of equipment such as tanks, tank linings, utensils, filter cloth, hoppers, chutes, etc., in cream of tartar manufacturing plants.

TABLE XV.—PLANT CORROSION TEST IN THE PRODUCTION OF TARTARIC ACID

CONDITIONS OF TEST.—In vacuum-pan evaporator concentrating pure tartaric acid to 57%. Temperature, 130° F. Duration of test, 20 days, during which equipment operated only 240 hours. No aeration, but agitation due to ebullition.

Material	Corrosion Rate Inch Penetration Per Year
Monel .. .. .	0-0005
Nickel .. .. .	0-0008
Inconel .. .. .	0-002a
Copper .. .. .	0-015
Chemical Lead .. .. .	0-060

a Local attack in the form of pitting to a maximum depth of 0-001 in.

### Maraschino Cherries

The data given in Table XVI were obtained in a syruping tank during the hot processing of Maraschino cherries in the presence of sulphur dioxide. Corrosion in this application does not appear to be a factor insofar as the materials tested are concerned, since all of them showed usefully low rates of attack. However, it should be pointed out that sulphur dioxide, even in dilute solutions, often produces rapid corrosion on many metals and, under the circumstances, it might be presumed that the syrup or cherry liquor used in the hot processing during the test had an inhibiting effect on corrosion of the materials investigated.

TABLE XVI.—PLANT CORROSION TESTS IN HOT PROCESSING OF MARASCHINO CHERRIES

CONDITIONS OF TEST.—In syruping tank with cherry liquor containing 40-1,000 ppm. of SO<sub>2</sub> at start. Temperature, 132°-140° F. Duration of test, 183 days, during which 25 batches were processed, each requiring about 4 days. Balance of time specimens were exposed to air at room temperature. No aeration or agitation reported.

Material	Corrosion Rate Inch Penetration Per Year
Monel .. .. .	0-0003
Nickel .. .. .	0-0025
Inconel .. .. .	0-0001
18-8 SS (Type 302) .. .. .	0-0001
18-8 SS (Type 304) .. .. .	0-0001
18-8 Mo SS (Type 316) .. .. .	0-0001

### Baker's Yeast

In the preparation of baker's yeast, as shown by the data given in Table XVII, all of the materials tested suffered pitting attack to some extent, although the overall corrosion rates as measured by weight loss were reasonably low. Mild steel, of course, was more seriously affected and would not be considered worthy of use in this service. However, some of the other materials, notably Inconel and copper, would possibly prove suitable in spite of the localised attack when the relatively long test period of 168 days is taken into account. Unfortunately, the stainless steels were not included in this test, but the Type 316 alloy should be considered as probably suitable for this service.



## Flour Bleaching

In the bleaching of flour, air-chlorine mixtures are used which together with small amounts of moisture usually present in the flour and the air creates a somewhat corrosive condition. The test results given in Table XVIII were obtained in such a process and indicate that Hastelloy C, lead and nickel are highly resistant to corrosion. Monel and Inconel were attacked at somewhat higher rates, with the austenitic stainless steels giving the poorest performance of the various materials tested.

TABLE XVII.—PLANT CORROSION TESTS IN THE PREPARATION OF BAKER'S YEAST

CONDITIONS OF TEST.—In liquid and vapour phases of process tank handling yeast cultures. Temperature, atmospheric. Duration of test, 168 days. Aeration good with practically no agitation.

Material	Corrosion Rate Inch Penetration Per Year	
	In Liquid	In Vapours
Monel .. .. .	0-0011a	0-0005d
Nickel .. .. .	0-0054b	0-0011f
Inconel .. .. .	<0-0001c	<0-0001g
Copper .. .. .	0-0022d	0-0038g
Tin .. .. .	0-0002a	0-0001a
Mild Steel .. .. .	0-0068e	0-0064e

a Local attack in the form of pitting to a maximum depth of 0-005 in.  
b Local attack in the form of pitting to a maximum depth of 0-008 in.  
c Local attack in the form of pitting to a maximum depth of 0-006 in.  
d Local attack in the form of pitting to a maximum depth of 0-004 in.  
e Local attack in the form of pitting too severe to permit accurate measurement.  
f Local attack in the form of pitting to a maximum depth of 0-003 in.  
g Local attack in the form of pitting to a maximum depth of 0-002 in.

TABLE XVIII.—PLANT CORROSION TEST IN AIR-CHLORINE MIXTURE USED IN FLOUR BLEACHING

CONDITIONS OF TEST.—Air-chlorine mixture consisted of 300 cu. ft. of air and 50 oz. of chlorine per hour. Average temperature, 80° F. Duration of test, 82 days, during which the specimens were exposed to the corrosive media only 128 hours. Good aeration and agitation.

Material	Corrosion Rate Inch Penetration Per Year	
	In Liquid	In Vapours
Monel .. .. .	0-012	0-003
Nickel .. .. .	0-003	0-011
Inconel .. .. .	0-011	0-011
18-8 SS (Type 304) .. .. .	0-044	0-022
18-8 Mo SS (Type 316) .. .. .	0-022	0-001
Chemical Lead .. .. .	0-001	0-0001
Hastelloy C .. .. .	0-0001	0-0001

## Condiments

Some laboratory and plant corrosion test data obtained in the processing or preparation of Worcestershire Sauce, India Thick Sauce, mustard powder and

TABLE XIX.—LABORATORY AND PLANT CORROSION TESTS IN THE HANDLING OF CONDIMENTS

TEST 1.—In steam autoclave during processing of Worcestershire Sauce. Temperature, 266°-275° F. Duration of test, 20 hours. No aeration or agitation.  
TEST 2.—In steam autoclave during processing of India Thick Sauce. Temperature, 266°-275° F. Duration of test, 21 hours. No aeration or agitation.  
TEST 3.—In mustard powder after grinding. Temperature, 70° F. Duration of test, 22 hours. No aeration or agitation.  
TEST 4.—In chile sauce containing red peppers and seasoning (acetic acid, etc.). Unseasoned at boiling temperature for 8 hours and aerated at room temperature for 23 hours. No agitation.

Material	Corrosion Rate, Inch Penetration Per Year				
	Test 1	Test 2	Test 3	Boiling	Room Temp.
Monel .. .. .	0-0033	0-006	0-0002	0-009	0-004
Nickel .. .. .	0-010	0-011	0-0027	—	—
Inconel .. .. .	—	—	0-0001	—	—
18-8 SS .. .. .	0-0003	0-001	<0-0001	—	—
18-8 Mo SS .. .. .	—	—	0-0001	—	—

chile sauce are given in Table XIX. These figures indicate the general suitability of Monel, nickel, Inconel and the austenitic stainless steels for use in handling these various condiments. However, caution must be exercised to avoid having particles of the salty wet solids remain in prolonged contact with the alloy surfaces, since pitting may be expected under such circumstances.

## Corn Syrup and Black Strap Molasses

A series of corrosion tests were made in the liquid and vapour phases of corn syrup during transportation in a tank car and during mixing in a tank, as well as in the liquid and vapour phases of blackstrap molasses during mixing. The results of these several investigations are shown in Table XX. The data indicate that the conditions are not significantly corrosive even to mild steel and cast iron which could probably be used to advantage if contamination by rusting were not a factor.

TABLE XX.—PLANT CORROSION TESTS IN THE HANDLING OF CORN SYRUP AND BLACK STRAP MOLASSES

TEST 1.—In vapour and liquid phases of tank car during transportation of corn syrup. Temperature, 80°-110° F. Duration of test, 85 days in vapour and 104 days in liquid. Little aeration and some agitation due to movement of tank car.  
TEST 2.—In vapour and liquid phases of corn syrup mixing tank. Temperature, 170° F. Duration of test, 114 days. Slight aeration and constant agitation.  
TEST 3.—In vapour and liquid phases of blackstrap molasses mixing tank. Temperature, 225° F. Duration of test, 44 days. Slight aeration and constant agitation.

Material	Corrosion Rate, Inch Penetration Per Year					
	Test 1		Test 2		Test 3	
	In Vapour	In Liquid	In Vapour	In Liquid	In Vapour	In Liquid
Monel .. .. .	0-0002	<0-0001	<0-0001	<0-0001	0-0013	0-0006
Nickel .. .. .	0-0006	<0-0001	0-0001	<0-0001	0-0011	0-0004
Inconel .. .. .	<0-0001	<0-0001	<0-0001	<0-0001	<0-0001	<0-0001
18-8 SS (Type 302) .. .. .	—	—	—	—	<0-0001	<0-0001
18-8 SS (Type 304) .. .. .	—	—	—	—	<0-0001	<0-0001
Copper .. .. .	—	—	—	—	0-0038	0-0017
Mild Steel .. .. .	0-0006	0-0007	0-0008	0-0010	0-0069	0-0060
Ni-Resist .. .. .	0-0012	0-0002	0-0004	0-0002	—	—
Cast Iron .. .. .	0-0046	0-0010	0-0018	0-0011	—	—

## The Steel Company of Wales Limited

THE first consignment of American machinery for the new works at Trostre has been discharged at Kings Dock, Swansea. It is from the United Engineering and Foundry Company of Pittsburgh, U.S.A., and forms part of the new cold reduction mill now being erected by the Steel Company of Wales Ltd., near Llanelli.

The largest individual items unloaded were the first six housings of the ten which will eventually be required for the new 5-stand mill. These housings each weighing approximately 97 tons, are 23 ft. high and two of them will be required for the erection of each stand. (A stand assembly when completely erected, consisting of housings, roll, chucks, shoe plates, and screw-down equipment, will weigh approximately 400 tons.) Other items in this first cargo were bed-plates weighing approximately 17½ tons, while the remainder consisted of screw-down plates, platforms, etc. A 100-ton floating crane was transferred to Swansea to assist in unloading.

The housings are stored at Swansea Docks until such time as they are required to be erected at Trostre, while the lighter loads were transported by road direct to the site of the new works where they are temporarily stored in the old Morfa Works which adjoins the site and which has been specially prepared for this purpose.

# Micro- and Macro-Deformations of Metals and Alloys under Longitudinal Impact Loads\*—Part II

By Dr. Georges Welter

(Professor of Applied Mechanics, Ecole Polytechnique, Montreal, Canada.)

## Testing Method II

In order to avoid the detrimental influence of this simultaneous bending and tension under increasing dynamic loads, the threading of specimen into the moving member was abandoned. As most testing machines used for impact testing are of the pendulum type, this loading system was retained for the second series of dynamic tests, with this fundamental difference, however, the specimen was not fixed in the hammer and did not move with the pendulum. On the contrary, it was rigidly fixed on the base of the machine so as to receive the blow of the hammer. This is shown in Figs. 12, 13 and 14, in all of which we see the guiding device of the specimen. A solid steel block A (5½ in. long, 5 in. high and 3½ in. wide) with a bore of 3 in. diameter (Fig. 13), is rigidly screwed to the base of the machine, supporting on one end in A the specimen by screws and having on the other end a light metal piston D gliding in the bore E. In the centre of this piston the specimen is fixed by means of a transverse F and a spherical seated screw G (Fig. 14). Besides this, the spherical, seated, self-adjusting transverse F (adjustable in an unloaded condition and, to save weight, calculated as a beam of equal resistance) has on both ends cylindrically shaped edges H which receive the blow of the



Fig. 12.

hammer. Further, the block supports a micrometer screw I, used to check the displacement of the piston by means of the rigid arm K. After each dynamic loading of the specimen the permanent deformation can easily be checked by this device with an accuracy of about 0.001 in. Moreover, this device has the great advantage of enabling us to measure the elongation of the specimen with sufficient accuracy after it has been stretched appreciably

and after the mirror extensometer L is no longer of any use.

It is understood that because of those fundamental changes in the loading system, the moving mass M of the machine had to be changed appreciably (Fig. 12). Difficulties had to be overcome, difficulties resulting from a change in shape and weight of the hammer, as well as from the displacement of the centre of percussion of the hammer which had to be made about 6 in. longer. Also, the striking centre must continue to correspond with the centre of gravity of the hammer in order to avoid energy losses by deformation and vibration.

The mirror extensometer, itself adjusted to the specimen, is represented in Fig. 15.

After a few preliminary tests had been made with this new device some important changes were found to be necessary. First, the weight of the modified hammer has to be reduced from 28 to 22½ lb., in order to maintain its relative harmony with the resistance of the specimen which had a fixed diameter of 0.3125 in. and with the different materials to be tested showing a wide range of the dynamic elastic limit (aluminium, 15,000 lb./sq. in. and medium steel, 100,000 lb./sq. in. static ultimate tensile strength). Furthermore, flat rods and fastening blocks of the mirror

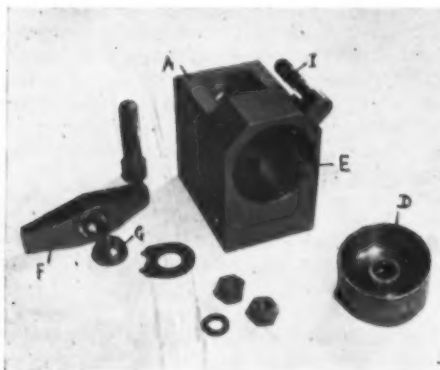


Fig. 13.

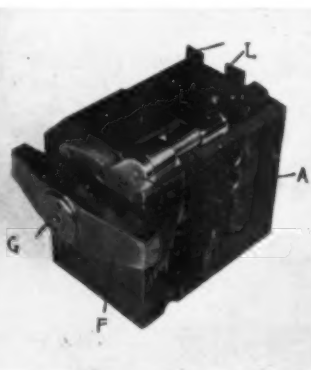


Fig. 14.

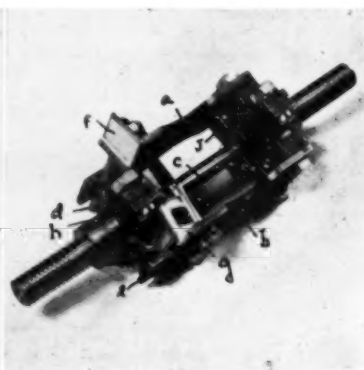


Fig. 15.

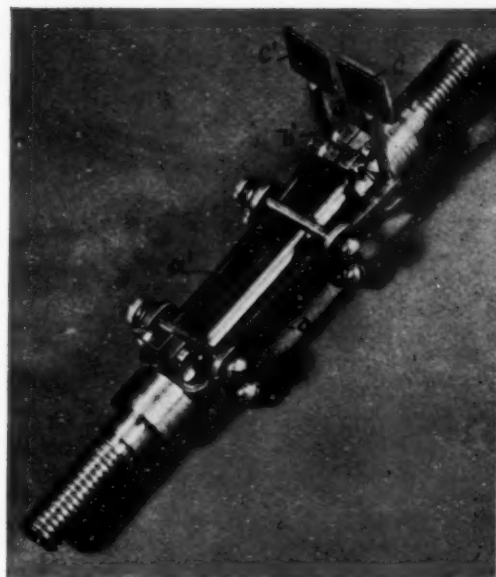


Fig. 16.

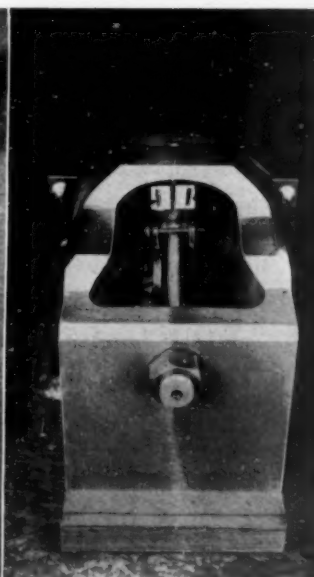


Fig. 17.



Fig. 18.

extensometer, shown in Fig. 15, were too heavy for instantaneous displacement under dynamic loads. Whenever their displacement for these relatively small elastic and micro-plastic deformations seemed extremely small, though due to the weight of the extensometer, a certain small amount of slipping on the specimen took place (especially in the testing of light alloys) and the results were erroneous. The weight of the whole device was therefore appreciably reduced and a more simple and, at the same time, more sensitive extensometer, as shown in Figs. 16, 17 and 18, was the result. The flat rods *a* and *a'* made of special steel (Fig. 16), very thin and small, were at one end, sharpened as a knife edge, gripping the specimen; on the other end, they supported in a sharp notch the prisms *b* and *b'* with mirrors *c* and

*c'*, placed in a specially divided, notched steel block *d* which was adjusted with a knife edge to the specimen. In order to achieve a higher accuracy in the test results, the gauge length of the extensometer was increased to 3.3 in. over the 3 in. length of the preceding device. Moreover, despite some difficulties encountered inside the guiding block, in order to find the necessary space for the mirrors which had to point over the lower edge of the block, the extensometer was adjusted on the specimen in the opposite direction, so that the flat rods of the extensometer were not displaced during the impact of the load. The mirror and the prism were fixed on the end near the loaded transverse *F* (Fig. 17), so that no part of the extensometer, except the prisms and mirrors *C* and *C'*, were in

movement during the impact of the loading. The transverse *F* itself was changed and the impact points *OO'* were shaped as a sphere and not cylindrically faced (Figs. 17, 18). Also the light metal piston was later on abandoned. In order to save some

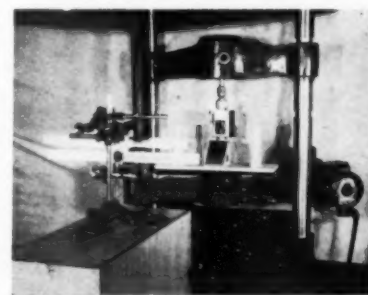


Fig. 18a.

TABLE III.—RESULTS OF DYNAMICALLY TESTED SPECIMENS

Material	Cycle of load 1—first 2—second	Dynamic test Diameter of specimen 0.325 in. Gauge length, 3.3 in.						Fig.	Static test Diameter of specimen 0.312 in. Gauge length, 3.3 in.					Fig.
		E ext. ft.-lb./ cu. in. perm. def.	E hammer ft.-lb./ cu. in. 0.003% 0.003%	E ext. 0.01%	Yield strength 0.2%	Def. total 1/1000 in.	Dynamic ultim. load appl. ft.-lb./ cu. in.		Load lb.	E lb./sq. in. <sup>9</sup> perm. def.	Yield strength 0.2%	Def. total 1/1000 in.		
Aluminium 2 S ..	1 2	2-4 3-4	(20) (25)	6-7 8-9	20 22	58 100	20 24	21	900	11,500	18,200	92	22	
Duralumin 17 ST ..	1 2	26-28 42-44	(50) (52)	25 46	—	55 100	63 78	23	1,600	20,800	40,000	173	7	
Magnesium Alloy 57S	1	50-52	(50)	65	—	102	108	24	1,100	14,400	35,700	160	25	
Steel—mild 1020 ..	1 2	50-54 40-42	(60) (52)	(64) (50-52)	—	67 100	95 100	26	2,500	32,600	41,000	99	10	
Steel—medium 1045	1 2	64-66 70-72	(64) (60)	72 77	—	81 160	120 126	27	3,000	39,000	51,500	140	11	



weight it was replaced by a solid disc P in which the specimen could glide in the centre hole Q during the impact of the loads (Fig. 18). This device outfitted with telescopes and scales and adjusted to the Baldwin Southwark testing machine, in order to carry out static tests, is represented in Fig. 18a.

The following structural materials have been investigated with this device adjusted to the Olsen pendulum impact testing machine: Aluminium, duralumin, magnesium and mild and medium steel. The dynamic tests have been made in the same manner as those previously described. The static load deformation diagrams, with the elastic and micro-plastic deformations

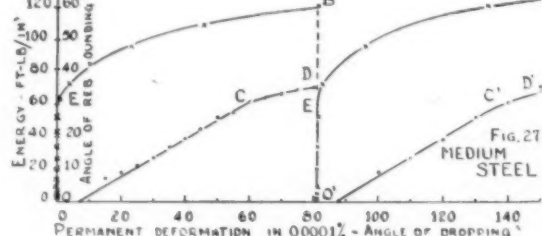
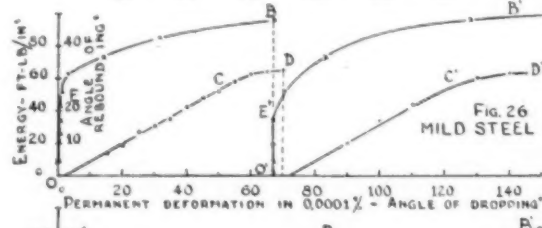
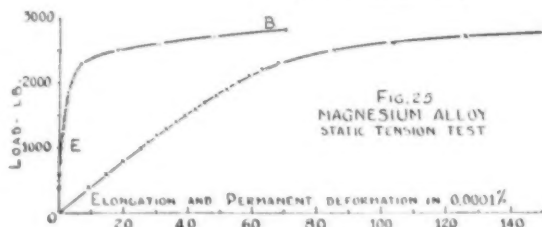
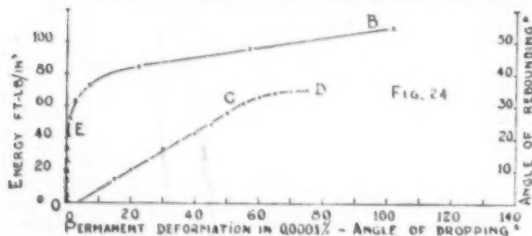
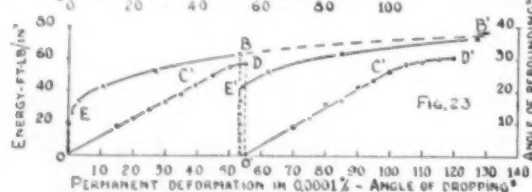
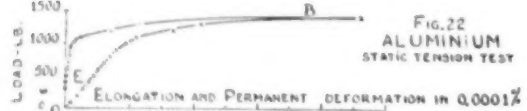
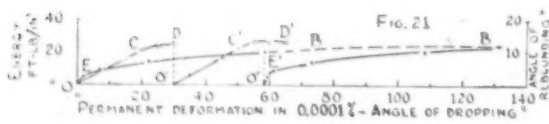
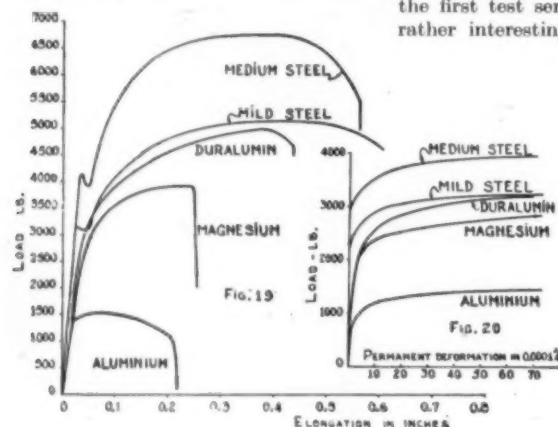
of these materials, are represented in Figs. 19 and 20.

In Table III and in Figs. 21, 23, 24, 26 and 27 are shown the results of the dynamically tested specimens; and in Figs. 22, 7, 25, 10 and 11 are given those of the static tests made with the special mirror extensometer used on the pendulum impact hammer. These results, which in the light of the previously described results of the first method are easy to understand, are in fairly close agreement with those of this first series of tests in which a somewhat less accurate extensometer was used. They show that the results concerning the elastic limit and the micro-plastic deformations are more or less equal to those found in the first test series (Table II). It is rather interesting to note that mild steel, during the second cycle of loading and due to its upper and lower yield point, shows a lower elastic limit than the virgin material (Fig. 26).

The method using the pendulum hammer and the mirror extensometer would have been considered satisfactory with

regard to the dynamic test results, if, after the dynamic loading, the cold stretched specimens would have remained completely straight, as they were before the test. Unfortunately, this was not the case; again, after a certain amount of cold stretching, the specimen did not remain straight. Despite the guiding device used in this method, which consisted in the action of a piston within a special axial boring, the specimens, after loading, were again slightly bent in the threaded heads which were fixed in the transverse by a spherical nut. As already stated, the displacement of the pendulum impact hammer does not take place in a straight line, but describes an arc of circle at each moment during its fall, the transverse, despite its self-aligning element and despite the guiding piston, is carried along on its curved trajectory, bending the head of the specimen more and more at each succeeding blow. Furthermore, due to the fact that there was an additional loss of energy whenever the cylindrical gauge length of the specimen was not seriously affected by the bending of the head, as well as to certain other uncontrollable effects (as for instance, higher friction in the piston), it was deemed advisable definitively to abandon the pendulum impact device for this kind of test.

(To be continued.)



# The Institute of Metals

## Annual Autumn Meeting at Cambridge

*In visiting Cambridge to hold its annual autumn meeting the Institute of Metals paid tribute to workers in all fields of scientific endeavour seeking fundamental truth and knowledge on which industrial technique and practices can be built. As the papers presented at the meeting show there is to-day an increasing tendency to apply fundamental knowledge to build up metals and alloys with pre-determined and controlled properties. The meeting is briefly summarised and attention directed to the technical sessions at which these papers were discussed.*

THE fortieth annual autumn meeting of the Institute of Metals was held at Cambridge on September 14-17, 1948. The initial meeting was held at the Art School, Benet Street, with Sir Arthur Smout, President, in the Chair, at which a Civic welcome was given by His Worship the Mayor of Cambridge (Councillor G. F. Hickson, M.A.).

### Civic Welcome

In welcoming members of the Institute, the Mayor referred to the Borough of Cambridge and stated that the Borough is older than its University, although it would not seem so to visitors because, apart from the churches, nearly all the old buildings to be seen are of the University or the Colleges. The older parts of the town have largely disappeared to make way for so-called modern improvements. The first reference to the town in written history is in the Anglo-Saxon Chronicle which states that two or three invading Norse chiefs and their armies spent some time in Cambridge, or rather in Grantabrig, as it was then known. It is probably the first place name in Teutonic language including the word "brig" or "bridge." By the time of William the Conqueror it was called Grantabridge, and the county Grantabridgeshire. In the time of Chaucer it was Cantabridge and in more modern times its present name of Cambridge.

Before there was a university at Cambridge—towards the end of the twelfth century—the Borough began to receive its first privileges of self-government, in the shape of charters given by various monarchs, many of which still remain in the possession of the Borough Council. The oldest dates from 1207, the second of two given by King John. Continuing, the Mayor mentioned that Cambridge was identified in the Civil War with Cromwell and his Puritan new model army, and Oxford with the King and the Court. He concluded by expressing great pleasure in welcoming members and their guests to Cambridge and hoped that the meeting would achieve the success they had in view.

The President, in thanking the Mayor for his welcome to the ancient borough and University of Cambridge, said that since the initial meeting of the Institute, held at Birmingham, it has been traditional that the Institute visit each autumn some centre of metallurgical activity. On this occasion new ground is broken since the meeting is being held in an academic rather than an industrial centre, and during the course of the meeting it was hoped to catch something of the atmosphere of Cambridge. In visiting this Borough the members of the Institute, consciously or unconsciously, are paying tribute to colleagues in all fields of scientific endeavour who are seeking that fundamental truth and knowledge on which to build our industrial technique and practices.

The development of metallurgy, he continued, goes back to ancient times and to our earliest recorded history.

Its progress through the ages has greatly affected everyday life, and it has left its mark on civilisation. During much of this time, metallurgy has perhaps been more of an art than a science. To-day it continues to be a mixture of art and science, but more and more in the future the application of fundamental knowledge will permit metals to be built up possessing pre-determined and controlled properties. Hence the Institute's interest in the University and ancient Borough of Cambridge, a centre of learning which has perhaps contributed more to fundamental knowledge of metals than any other centre in the world.

### Welcome to Overseas Delegates and Members

The President, in greeting members at the initial meeting, said he particularly welcomed the six official delegates from the Association Technique de la Première Transformation de l'Acier et des Metaux Non-Ferreux of Paris. He also expressed pleasure at the presence of Dr. W. Boas, from Australia; Professor R. E. de Strycker, from Belgium; Professor G. Letendre, Dr. N. W. E. Phillips and Mr. R. H. Rimmer, from Canada; five or six other delegates from France; delegates from India and Switzerland, including Professor A. von Zeerleder, from Switzerland; and Dr. F. C. Frary, Mr. Irving Rossi, Dr. George Sachs and Dr. Cyril S. Smith from the U.S.A. Cordial greetings were also extended to Mr. and Mrs. Shaw-Scott on this the fortieth anniversary of Mr. Scott's appointment as first secretary of the Institute.

### Nominated for Vacancies on the Council

The Council has nominated to fill vacancies:—

*President:* Sir Arthur Smout, J.P.

*Vice-Presidents:* Major C. J. P. Ball, D.S.O., and Dr. C. J. Smithells, M.C.

*Members of Council:* Mr. E. A. Bolton, M.Sc., Mr. C. H. Davy and Dr. A. G. Quarrell.

### TECHNICAL SESSIONS

Following the business meeting, time was allocated to the presentation and discussion of papers, the first of which was a discussion on the subject of the Micro-Hardness Testing of Metals, based on a paper by E. Wilfred Taylor. A further paper on "The Measurement of the Damping Capacity of Metals in Torsional Vibration," by G. A. Cottell, K. M. Entwistle and F. C. Thompson was subsequently presented and discussed. Two further papers were presented and discussed at the technical session held the following morning, "The Effect of Crystal Arrangement on 'Secondary Recrystallisation' in Metals," by J. S. Bowles and W. Boas, and "Observations on the Annealing Characteristics of an Aluminium-Copper-Magnesium Alloy" by Maurice Cook and T. L. Richards, and in the following notes an effort has been made to present the salient features of these papers and a digest of the discussions which resulted.

## MICRO-HARDNESS TESTING OF METALS

By E. WILFRED TAYLOR, C.B.E., F.Inst.P

**A**LTHOUGH there are some eight American and Continental types of micro-hardness testing machine in existence, that described by the author is the first British micro-hardness tester to make its appearance. It is a direct loading machine, designed for use with an inverted-type metallurgical microscope. Briefly, it consists of a carefully balanced lever arm, pivoted on a ball bearing fulcrum which is part of a base plate fixed to the microscope stage. The specimen is attached, face downwards, to the end of one arm of the lever, whilst the other arm carries adjustable weights for counterbalancing after the specimen is fixed in position. Weights are placed on a small platform above the specimen and an impression is made by raising the objective, containing the diamond indenter, by means of the fine focussing screw, until the specimen is lifted slightly as indicated by a warning light. Examples are given of its use in investigating the hardness of individual microstructural constituents, the depth-hardness curve of a nitrided case, the hardness of thin foils and of electroplated deposits.

### Discussion

In presenting the paper, Mr. TAYLOR mentioned the difficulty of producing a satisfactory pyramidal diamond indenter. With such low loads as were a feature of micro-hardness testing, only the extreme tip was in use and it was very difficult to work up the diamond to the high standard required for the production of a perfect impression. One difficulty encountered was that of ensuring that the four facets meet in a point and, as a possible means of overcoming that difficulty, Mr. Taylor tentatively suggested using a diamond which made a triangular impression, as the three facets must meet in a point.

As all fine-focussing mechanisms exhibited some degree of backlash, provision was made for lifting the specimen from the indenter by means of a chain attached to the other end of the lever, rather than risk further indentation on reversing the fine-focussing mechanism.

PROFESSOR H. O'NEILL welcomed the appearance of a British micro-hardness tester and hoped that it would quickly get through its teething troubles. He suggested such machines would be more correctly named "hardness micro-testers." Such testers appeared to be of interest in studying brittle and hard substances, thin material, microconstituents and orientation effects in single crystals. The author had shown variations in hardness from 129 to 183 on a crystal of phosphor bronze depending on the orientation of the diagonals of the diamond, and it was evident that a code of testing would have to be drawn up.

Referring to the question of the hardness of microconstituents, Professor O'Neill mentioned the value of testing for various times to determine the flow properties. He was puzzled by the hardness value of 200 kg./sq. mm., given for both ferrite and pearlite. The generally accepted values were 85 for ferrite, 200 for pearlite and 750 for cementite.

The method of removing the load by pulling the chain did not appeal to him and he suggested that some other method should be devised to make the British machine second to none. The danger of errors due to inertia and friction was serious and Professor O'Neill referred to the instrument made by Gerschig which attempted to remove the effects and enable tests to be made on electro-deposited copper, 15 microns thick.

Hardness values increased progressively as the load decreased. Bergsman was satisfied that it was not a result of surface strain-hardening. Creep was not a likely cause and it was probably due to elastic recovery. Further work was necessary on such points and Professor O'Neill looked forward to the author's instrument being used in such researches.

MR. L. ROTHERHAM said that, although his approach was from the industrial angle, his conclusions were, in part at any rate, the same as Professor O'Neill's. Although spring-loaded machines needed greater care in operation, he felt that, as they would mostly be used in research work, the operator should be capable of maintaining a spring-loaded machine in order—he had to maintain a projection microscope in good order. On the other hand the direct-loading device had many advantages, the only disadvantages being the inertia and friction in the bearings. Inertia troubles seemed to be absent at loads above 25 gm. and he thought that at low loads the introduction of a device such as the soft-spring or sorbo-rubber used to support the loading lever in the Vicker's machine, would eliminate inertia troubles due to careless handling. In the recent Vicker's machine, friction on the ball-bearings was negligible down to 1 kg. loads and he thought that with careful maintenance a good bearing should not introduce friction troubles.

Mr. Rotherham asked what method had been used in polishing the cutlery-type stainless steel used for some of the tests, as he had found it almost impossible to polish such a material mechanically without softening the surface layers. In conclusion, he agreed with Professor O'Neill that the machine would be welcomed by British metallurgists.

DR. W. HUME-ROTHERY felt that too often instruments were not discussed by the people who were going to use them, he therefore welcomed the decision to discuss the paper before the Institute.

Even when all precautions were taken to avoid false results, hardness still seemed to be a profoundly unsatisfactory quantity. In ordinary macro-hardness testing, the effect of individual crystals was averaged but, as Professor O'Neill had pointed out, with micro-hardness testing the orientation of the crystal had to be considered. This question of orientation offered a fine field of research to see to what extent the instrument could be of use. He was attracted to it by reason of its possibilities in connection with the identification of phases in equilibrium work, in cases where ordinary etching methods were unsuitable. This would necessitate taking tests at various orientations on a number of crystals of each phase, in order to ensure that the difference between two phases was outside the limits of variation due to orientation alone.

In conclusion he thought that the instrument required further investigation and that some of the author's conclusions were rather in advance of what was justified.

DR. T. B. CROW said that most metallurgists, at some time or other, had wished for such an instrument as the author had described. It would have been very useful to him some twenty years ago for the identification of interfacial alloys, in soft soldering of copper, by comparison with known alloys.

He was interested in its application to the routine control of thin material, of the order of 0.006 in. thickness and under. It might also be useful in determining the existence, or otherwise, of skin hardness in cold worked metal. In connection with orientation, Dr. Crow referred to some work by Hinsley and himself, in which they noted the



difference in shape of ordinary Vickers impressions on heavily cold-rolled metal, depending on the direction of the diagonals relative to the direction of rolling.

The danger of spurious values resulting from work-hardening and polishing was shown recently in *Nature*. Abrasion increased the hardness of a chrome-molybdenum steel to a depth of 3.5 to 6 $\mu$ , depending on the degree of abrasion. As the depth of a micro-hardness impression would be very much less than that, the value measured would not be the true hardness of the material, but rather that of the abraded layer.

Whilst there were undoubtedly difficulties in carrying out the tests, and it might be some time before absolute accuracy was achieved, there was a field of usefulness for comparative values. His company was often asked to match the temper of extremely thin materials and a micro-hardness tester gave them a means of doing so.

DR. J. C. CHASTON referred to the excellent studies of micro-hardness testers which had appeared in the American literature, in which several difficulties were described. Inertia effects were observed with the original Tukon machine and he felt that users would need a good deal of reassurance on that question. A second trouble mentioned was the effect of vibration—care would be necessary in avoiding it in a hand-operated machine. A slight rocking of the indenter as the load came on was observed in the American machines and he noted that, in some of the photo-micrographs illustrating the paper, the impressions lacked symmetry. He wondered whether they had been made on a different machine. Dr. Chaston asked whether the pyramid diamond impression was easier to read than that of the Knoop diamond as that reason had been given for the reversion to the pyramid type in an American machine. He thought the author's suggestion of a three-cornered indenter to be worthy of consideration.

With regard to the constancy of hardness with various loads, Campbell, in an American paper, said that the hardness decreased with light loads due to the inaccuracy of the tip of the indenter. The surface layer of the specimen was important and he thought that electro-polishing might be necessary.

DR. H. K. HARDY who was concerned with testing very small hard components made from hypodermic tubing, was interested in the reproducibility of results. Some investigators took as many as 20 impressions with two observers before quoting a hardness figure, but he could only make three impressions per specimen. He confirmed that it was more difficult to read the impression of the Knoop indenter than that of the pyramid diamond, but even there, with tiny impressions, there was some difficulty. Any information on the effect of polishing, and of varying degrees of etching, on hardness values would be very valuable.

DR. E. OROWAN referred to the apparent increase in hardness with low loads. It might be due to a number of causes but, although it might not be the cause in the cases observed, there was a fundamental reason why an increase would be expected, as soon as the indentation dimensions, divided by the inter-atomic distance, became as small as the ratio of the modulus of elasticity to the yield stress. In order to produce plastic glide, adjacent glide planes must move by at least one inter-atomic distance and, with very small specimens, the elastic distortion at the usual yield point would not be sufficient to cause that displacement. In such conditions, no plastic glide could occur and to produce it, it would be necessary to apply a shear stress much higher than the normal yield stress, so high that the elastic distortion, produced in the material before glide,

was sufficient to give, after glide, when the elastic stresses had disappeared, a displacement of at least one inter-atomic distance.

### Author's Reply

MR. E. WILFRED TAYLOR, in reply, referred to the question of orientation and said that, whatever the explanation, it was a fact that some impressions were square, some had concave sides, some convex sides and some were almost circular, and he agreed that it would be necessary to evolve some code of practice. Mr. Taylor agreed with Professor O'Neill that it was possible to study the flow properties, as the impression size did vary with time on some materials. In some cases it was possible to observe a very beautiful ripple effect beyond the edge of the impression. He knew the question of the hardness of ferrite and pearlite would crop up—perhaps he would have been wiser to say that the figures obtained were as stated rather than the hardness. In attempting to measure the pearlite hardness, the plates seemed to shatter and he thought they were merely getting another test on the ferrite.

Professor O'Neill had not liked the method of removing the load by pulling the chain. On the machine they had seen the previous evening, it was not necessary, but they had to cater for the equipment being used on microscopes on which the slow motion mechanism was not perfect. He was pleased that no objections had been raised to the triangular diamond.

With regard to constancy of hardness at low loads, they had stopped at 25 gm. because they thought surface hardening had caused the increase at lower loads. He thanked Dr. Orowan for the explanation he had given of what might be the real cause.

Inertia effects were a possible source of error, but a safe speed could easily be determined and they recommended 10 $\mu$ /sec., which could easily be controlled. Vibration had also been mentioned; that could be troublesome and in the tests on stainless steel shown, one impression of a set was bigger than the others due to a water pipe knock—it was essential to avoid vibration by a good foundation.

The reason for some of the impressions lacking symmetry was that they were made with an early imperfect diamond. They had not done sufficient work to say when mechanically polished and unetched surfaces were safe to use.

Dr. Hardy had referred to hypodermic tubes—they had done several tests on them without difficulty. On the whole the results showed reproducibility to be good but he would carry out tests using a large number of impressions and arrive at a figure for the probable mean deviation.

In conclusion, Mr. Taylor expressed his thanks for the interest shown in the paper as evidenced by the discussion.

### THE MEASUREMENT OF THE DAMPING CAPACITY OF METALS IN TORSIONAL VIBRATION.

By G. A. COTTELL, K. M. ENTWISTLE, M.Sc.,  
and Prof. F. C. THOMPSON, D.Met., M.Sc.

FOR materials of low damping capacity, such as Duralumin, mechanical methods of testing give values which may be more than a hundred times as great as those obtained using physical methods. There are three possible explanations: (1) That there is a serious error in one of the methods; (2) that the methods are measuring different properties; or (3) that there is a marked frequency sensitivity. The paper presents the results of an investigation to determine which explanation is correct. The machine on which the mechanical

tests were carried out was of the Föppl-Pertz type, and by means of a careful isolation of the possible sources of error, followed by a redesign of the machine, the measured damping capacity was reduced from some 500 times the lowest value measured by physical methods, to twice that value. The most serious energy losses in the machine arose from lack of frame rigidity, the high air-friction loss, inseparable from a rectangular bar-type of inertia member, inadequate gripping of the specimen and the use of a ball-type steady bearing. In the modified design the steady bearing is discarded as soon as oscillation commences. By suitable modification of the faces of the grip, the loss associated with gripping a square-shanked specimen can be reduced to a low value, but shanks of taper cylindrical form, expanded into the machine components, are much to be preferred. The air-friction loss associated with a swing bar inertia member is prohibitively high and the only satisfactory solution is to design it in the form of a solid of revolution of smooth surface finish and free from avoidable irregularities of form. Tests at reduced pressures indicate that the air loss can be considered virtually absent at pressures of the order of  $10^{-3}$  mm. of mercury.

The investigation confirms that the physical and mechanical methods are, in fact, measuring the same property, and shows that for aluminium alloys, at least, results of the same order can be obtained by the two methods, provided the apparatus is correctly designed.

It is emphasised that the work described has been carried out on specimens of very low damping capacity, and it does not necessarily follow that materials of high damping capacity will show a substantial decrease, as compared with published values, when tested in a modified form of machine as described in the paper, because the losses in the machine would then have a proportionately smaller effect.

While the agreement between the physical and mechanical determinations supports the belief that the damping capacity of Duralumin is not seriously frequency sensitive, it has not been established that it is completely independent of frequency and further work is in hand with the object of obtaining conclusive evidence on this important aspect of damping capacity testing.

In an Appendix to the paper, Dr. G. L. J. Bailey, Head of the Physics section, B.N.F.M.R.A., proposes a method of treating experimentally, recorded decay curves, so as to estimate the specific damping capacity at any measured amplitudes within calculable limits of error.

### Discussion

MR. G. A. COTTELL in presenting the paper drew attention to the fact that the strain values for the new machine, both in the text and in the diagrams, were just twice the correct values, due to the authors having disregarded the fact that a reflected ray of light is deflected through twice the angle of rotation of the reflecting surface. This did not alter significantly either the test results or the conclusions.

In the ensuing discussion, tribute was paid to the rational way in which the authors had tackled the problem, refusing to be led astray by any preconceived ideas and carefully isolating and eliminating the various sources of error.

DR. R. F. HANSTOCK pointed out that at the time Föppl presented his paper to the Iron and Steel Institute in 1936, it was generally believed that, whilst materials differed considerably in damping capacity, values of less than 0.5% were seldom found at stresses of a few tons/sq. in., and it was therefore thought that the damping capacity of a

material could be an important factor in the control of resonance vibration. Following the development of physical methods of testing it became apparent that for aluminium alloys, at any rate, the values given by the Föppl-Pertz machine were far too high and the authors' work had confirmed that, provided adequate precautions were taken, there was no serious discrepancy between physical and mechanical results. He wondered, therefore, having perfected the instrument, did the authors consider that the original need for it, as envisaged by Föppl, still existed, or were there any reasons for supposing that the measurement of damping capacity was desirable from a practical point of view.

DR. H. SUTTON considered that the authors had done a very valuable piece of ghost-laying work and had shown clearly and definitely the importance of particular factors, which had been the subject of doubt in the minds of those interested in damping.

Many people were interested in vibration problems in relation to high speed air current effects, and it was gratifying to know that aero-dynamic damping can have such a powerful effect. He was pleased to hear that work was proceeding on the question of the influence of frequency and he looked forward to seeing the results of that work.

Others present were more competent to speak on the use of damping as a means of studying the changes going on inside materials, and he hoped Dr. Cyril Smith of Chicago would have something to say on that aspect.

MR. L. ROTHERHAM thought the author's statement that "the measured damping values obtained with a machine based on the Föppl-Pertz design are no indication of the true damping capacity of the material under test"—was rather sweeping. For instance a number of improvements made in the author's machine were used throughout in the experiments made by the late Dr. Hatfield and himself. They had the machine clamped to a large mass, no steady bearing was used and results were never accepted unless they could be reproduced on turning the specimen through 90° or upside down, and the torsion pendulum was suspended from the top instead of the bottom. Even so, they had trouble from bending of the specimen, and had he not seen Mr. Cottell in action, he would have asked how it was prevented in this work.

Despite the amendment made by Mr. Cottell in presenting the paper, Mr. Rotherham thought the comparison he had made, showed that their results were comparable with those of the authors, after completing the modifications to the original machine, and before eliminating air-friction losses.

The interesting thing about damping capacity was its variation with temperature and frequency. He was glad that the authors proposed to study the effect of frequency on the damping capacity of Duralumin or RR56, because, as it stood at the moment, it was rather misleading to say the two methods were necessarily measuring the same property. He could not emphasise too strongly that a test at 149 cycles/min. was not the same as one at 48,240 cycles/min.—in the present case they happened to give like values but in other cases they might differ by a factor of 10 or 100.

THE CHAIRMAN then invited Dr. Cyril Smith to take part in the discussion.

DR. CYRIL SMITH (U.S.A.) said that he had nothing to add to the discussion on the paper, but he would like to refer to the work being done at Chicago. Dr. Zener was responsible for the work on internal friction, which had been done with extremely simple apparatus and which was directed at an understanding of the happenings inside the

metal rather than at engineering problems. It was only by a study of the effect of temperature and frequency that one could understand the various kinds of factor responsible for internal friction. Dr. Zener had shown that there were at least six different sources of internal friction. They were: (1) That due to gross thermal currents in the sample, i.e., flow of heat from one part to another of the sample as a whole; (2) the similar effect between two adjacent grains which would be differently strained and would change with temperature accordingly; (3) that due to grain boundary effects, i.e., to viscosity in the grain boundaries; (4) that due to the migration of twin boundaries, particularly in tetragonal materials; (5) that due to migration of elements in substitutional solid solution and; (6) the similar effect tied up with the movement of minor constituents in interstitial solid solutions.

This all added up to the fact that internal friction was a useful scientific tool, and he looked forward to the answer to the question put by an earlier speaker, as to the engineering use of the figures.

Dr. C. J. SMITHELLS said that at the time the Research Council of the B.N.F.M.R.A. discussed whether they ought to take an interest in damping capacity, the results being obtained varied by about 1,000-1, according to the method of measurement, and there was, consequently, some justification for those who doubted its existence. Looked at from an engineering point of view, if the damping capacity were of the order of 1%, it might be of interest to designers, but it was doubtful whether values of 0.001% had any practical significance. Also considering the difficulty of getting rid of extraneous damping in any machine used to measure it, it was obvious that with any machine built, there would be so much damping from mechanical joints that intrinsic damping capacity would hardly come into the picture.

They realised that it was likely to be useful as a research tool and it was felt that the Association should support the work. The mechanical and physical methods being in such close agreement, there was no doubt that damping capacity varied with structural changes in the metal. To be of any use as a tool, it must be reliable and the authors, by their work, had removed any doubts on that aspect. They had gone further and produced results which he hoped would be published, in due course, which showed how useful a tool it could be.

Dr. Smithells said he would like to ask Professor Thompson whether he regarded damping capacity as an important property of an engineering material, or as a research tool.

Dr. G. L. J. BAILEY thought that engineers had suffered a blow at that complacency which left the more difficult vibrations, which occurred in their machines, to be catered for by the damping capacity of the material, as the values were certainly, at low stress amplitude, a good deal less than they had thought, and the chances of building up vibrations of larger amplitude correspondingly greater. The work of Hanstock and Murray had shown that increased damping at higher stresses might well mean that the material had already begun to fail.

The authors' experience of grip losses suggested that the study of materials and methods of making joints might be useful from the engineering point of view. Dr. Bailey referred to the question of vibration history. Below a certain stress amplitude, the damping capacity was independent of the number of cycles undergone, and would not change unless the structure changed, e.g., by ageing. On the other hand if the stress were high enough to disturb

the structure, the damping value depended on the vibration history of the specimen. The intrinsic value was the proper one for the study of grain size and the high amplitude one for the study of fatigue characteristics.

Referring to the use of damping capacity as a quick non-destructive quality control test, Dr. Bailey said it might well be that there was a field for the empirical study of intrinsic damping capacity as a function of the specimen of the material and its condition, leaving explanations until later, and that from such work useful quality control tests would emerge. In such work, the measurement of damping versus frequency at all amplitudes would be more useful than that of damping versus amplitude at a particular frequency. He thought the authors would agree that the machine had some way to go before it could be used for quick non-destructive testing.

In conclusion he asked whether the authors would expect to find the frequency-dependent contribution to the damping, as a result of intergranular thermal currents, in the case of Duralumin, since aluminium is elastically almost isotropic.

### Author's Reply

Dr. K. M. ENTWISTLE, in reply, said he would deal with the three main points which had been raised. With regard to the effect of frequency, they had found in studying the effect of the grain size of  $\alpha$ -brass on damping capacity that, as Dr. Zener predicted, there was a contribution from inter-crystalline thermal currents. That was important as it meant that in any anisotropic material, in torsional vibration, there would be a contribution to the damping capacity which was frequency sensitive. With Duralumin, whose elastic anisotropy was small, they would get a small but definite frequency effect. That would partially explain the differences between the results on the new machine and those by physical methods at higher frequencies.

Replying to Dr. Sutton's remarks on the aero-dynamic damping resulting from vibration in the atmosphere, Dr. Entwistle pointed out that the magnitude was not large. He did not really think that damping could be relied on to take care of resonant vibration; the solution of the problem lay in avoiding resonant frequencies.

With regard to Mr. Rotherham's remarks, he would point out that the statement to which Mr. Rotherham took objection was qualified by the phrase—"in the case of materials of low damping capacity." No conclusions were drawn for materials of high damping capacity.

The authors were all aware of the fine work done at the institution with which Dr. Smith was associated and Dr. Entwistle felt that when they considered the results of the small machine, of the six factors which Dr. Smith enumerated, the contribution from intercrystalline thermal currents would be the predominant one.

Much work was needed on the two aspects of damping capacity in relation to structure, one considering the effect of high vibrational strains and the other using low stress measurements to indicate the condition of the material. He and his colleagues were concentrating on the latter.

### THE EFFECT OF CRYSTAL ARRANGEMENT ON "SECONDARY RECRYSTALLISATION" IN METALS.

By J. S. BOWLES, M.Sc., and W. BOAS, Dr.-Ing.

"SECONDARY recrystallisation" is the term applied to the process whereby, after normal grain growth in recrystallised metal has stopped or is proceeding very slowly, a number of grains grow rapidly and consume the primary recrystallised grains in the



same way as they did the grains in the cold-worked material.

In the present work the authors set out to find the effect on secondary recrystallisation of the mode of arrangement of the crystals, by studying the phenomenon in specimens which had been given the same amount of deformation by two types of rolling. They were straight rolling and what the authors term compression rolling, in which the rolling direction is changed at each pass. Straight-rolled specimens possessed the usual type of preferred orientation, while the compression-rolled specimens possessed fibre structures. The experiments were carried out on copper, silver and two grades of aluminium.

It was found that secondary recrystallisation can occur regardless of the mode of arrangement of the crystals, but that it occurs more rapidly the greater the similarity between their orientations. It is suggested that this is caused by the difference in the ease with which the secondary crystals can grow, rather than in their tendency to grow.

It was also found that neither recrystallisation nor secondary recrystallisation alter the mode of arrangement of the crystals existing after deformation. It is shown that the existence of such an orientation relationship is not necessarily evidence in favour of Burgers' "nuclear spot" theory.

### Discussion

DR. E. OROWAN, in opening the discussion, outlined the general view of recrystallisation. There were four physical processes which, alone or in combination, governed the shape and size of grains obtained on annealing a plastically distorted material. They were: (1) Primary recrystallisation; (2) grain growth; (3) secondary recrystallisation, and (4) polygonisation. On continuing to anneal severely cold-worked aluminium, after primary recrystallisation had occurred, movement of the boundaries constituting normal grain growth would follow and then, suddenly, without intervening cold work, a number of grains would grow rapidly and consume the primary recrystallised grains in the same way that the primary grains had consumed the cold-worked grains. That was secondary recrystallisation. The latent energy of cold working was obviously the driving force of primary recrystallisation, but what caused secondary recrystallisation? There were two schools of thought. In the first it was believed that the high degree of preferred orientation, due to the large amount of cold-work, often remained after recrystallisation, and that when the primary recrystallised grains had almost the same orientation, there was a tendency for them to fuse completely. The second school believed that after primary recrystallisation, the material was not quite free from residual stresses and that they provided the driving force. The authors had tried to determine which hypothesis was correct. They produced in one group of specimens half-alignment only; one crystal axis being aligned and the crystals for the other axis being at any orientation; this was effected by a compression carried out by rolling with varying directions of rolling. Only in the case of the completely aligned specimens could the crystal orientations have been nearly identical and if secondary recrystallisation were observed in both, the fusion hypothesis was untenable, but that did not necessarily mean the residual stress hypothesis was correct—there were other possibilities. The authors had also determined the orientation of the secondary grains and as their results differed from the two previous differing

determinations, it seemed there was much to be learned on the governing factors.

Although the authors had produced secondary recrystallisation in both fully and uniaxially aligned specimens, they seemed to be of the opinion that full alignment exerted a favourable influence. The position was not at all clear, however; with copper and silver it was so, but with aluminium the reverse was the case.

There was a further difference between the two sets of specimens, in that there was probably about 15% more cold-work in the straight rolled material than in the compression-rolled material.

Dr. Orowan then referred to the lack of homogeneity in the deformation resulting from rolling. The skin was much more deformed than the middle of the specimen. It had been shown, by Beckman and Polanyi, that there were cases in which the material was not capable of producing nuclei for recrystallisation because of the small amount of cold-work. Recrystallisation could occur, however, if a nucleus could form in a more severely deformed part and grow into the less worked region. That was important in practice as slightly rolled material could be recrystallised by nucleation in the more severely worked skin. In research work it might be necessary to etch off a thick layer from the surface before annealing. He did not think such factors were of importance in the work described by the authors.

DR. MAURICE COOK said that little of immediate practical value had been added to the simple generalisations of 30 years' ago on the subject of recrystallisation. Recent work had been directed to seeking out explanations, and he felt that some of the work had been made unnecessarily complicated by a regrettable tendency to premature theorising on insufficient evidence, and to a confused use of terms and expressions. He considered that the phenomenon dealt with in the paper was not really recrystallisation at all, as ordinarily understood, but rather was abnormal grain growth.

Dr. Cook then referred to his own work on annealing copper, in which, by relatively heavy cold-rolling and a high final annealing temperature, they were able to produce—in straight rolled material—very large crystals with acicular characteristics. There was little doubt that the formation of crystals of that type was associated with the single texture structure. By cross-rolling, what appeared to be a different type of abnormal grain growth occurred on annealing, but the mechanism was not yet understood. Only copper of high purity showed the effects, less pure coppers subjected to the same treatment did not grow abnormally. It was not surprising that the authors had found an orientation in their acicular crystals which was different from that quoted by Richards and himself as their crystals were almost equiaxed. They were developed in copper strip of large initial grain size, cold-rolled with 75% reduction and annealed at 800° C.

The authors had established that the orientation of the large acicular crystals differed from that of the single texture structure in which they grew, the difference being equivalent to a rotation of some 30° on octahedral planes. Richards and himself, on brass strip, had found it to be equivalent to rotation and twinning on certain octahedral planes. Dr. Cook considered that the re-orientations were more likely to occur by atomic rearrangement than by actual rotation of block units.

DR. J. C. CHASTON agreed with Dr. Cook that secondary recrystallisation was a misleading term and he felt there was no definite proof that it was a new phenomenon. More

particularly in ferrous metallography, the presence of particles of impurity, e.g., alumina, were regarded as playing a part in exaggerated grain growth by stopping the crystals growing as fast as they would; after a time the resistance disappeared and secondary recrystallisation occurred. Similar effects had been found with a beryllium copper alloy with cobalt additions. In view of the effect of impurities it would be valuable if the authors would describe their materials more fully than by saying, "99.5% copper" or, "silver sheet 999 fine."

Referring to Dr. Orowan's remarks, Dr. Chaston said he had not understood that the authors had restrained spread in straight-rolling and he did not, therefore, see why there should be a 15% difference in applied stress in the two methods of rolling.

Knowledge of recrystallisation was still very sketchy and papers, such as that presented by the authors, which made one think about it, were greatly to be welcomed.

Dr. H. LEPP (France) said one thing had struck him in connection with recrystallisation, and that was that he had never seen in any paper an attempt to express the energy, in calories, required to carry out the various processes and he felt it would be valuable if that could be done.

Dr. F. C. FRARY (U.S.A.) said he thought they would agree with Dr. Cook that, after recrystallisation, only grain growth occurred. He sometimes wondered whether the so-called appearance of new grains, on examining a section, was nothing more than growth in another direction, and whether there were not dangers in attempting to determine, from a single plane, a process going on in three dimensions.

Dr. CYRIL SMITH (U.S.A.) said that secondary recrystallisation or secondary grain growth, as he preferred to call it, only occurred when ordinary growth had stopped or was proceeding at an extremely slow rate. It was generally observed on thin sheet, where grain growth almost came to a standstill when the grain size became commensurate with the sheet thickness. It seemed, to him, that secondary grain growth might be the result of two of Dr. Orowan's processes, the normal surface tension effect, such as causes ordinary growth, and the polygonisation effect. If there were a possibility of the mosaics in adjacent crystals moving round, once the whole structure had become stable, it might possibly happen, once in a while, that two adjacent mosaics, separated by a grain boundary, matched exactly. In that case there would be a hole in the grain boundary and surface tension would pull it out, changing the angles at the side and resulting in a large grain which could grow in the ordinary way. Such ideas were mere conjecture, without any supporting evidence, but it was possible that something of that sort happened.

Dr. C. J. SMITHELLS, referred to the tungsten lamp filaments, with about 20 crystals to their metre length, which were produced controllably by the million. He agreed that exaggerated growth was very dependent on the presence or absence of impurities, and that the process was simply grain growth. Immediately after recrystallisation of drawn tungsten wire, there was no preferred orientation at all, so that there seemed to be some factor which he thought was largely an effect of restraint due to the presence of impurities, which allowed certain grains to grow abnormally.

Dr. L. B. PFEIL said that he had been interested in the growth of large grains in iron, and he found that it was only by selecting certain varieties of low carbon steel that he stood any chance of producing large grains. It seemed as if one had to hold the grain size small until a relatively high temperature was reached and then let it go. He came to the conclusion that something in the nature of finely

divided inclusions was necessary to facilitate the process. Platinum produced by powder metallurgy required a much higher temperature for recrystallisation after cold-work than did ordinary platinum, and it was thought that pores in the metal held up the grain growth. When it did recrystallise, sintered platinum produced large grains.

Mr. F. H. MALHERBE said he had been working on the secondary recrystallisation of aluminium, and at the stage when large grains were growing, he had found cases where there were large gaps in the grain boundaries, possibly as a result of the action suggested by Dr. Smith.

Mr. J. W. JONES said he thought they ought to distinguish between the various stages in the recrystallisation process. The primary recrystallisation reached an end when, from various nuclei, a completely new set of crystals were formed. Grain growth then took place, and in a short time the small crystals had absorbed or been absorbed by their neighbours. It was easy to see how grains grew from a nucleus into a strained and collapsing grain, but he had no theory as to why a recrystallised grain grew into its neighbour. There were two phenomena: recrystallisation, which was limited to the growth of a new grain into strained adjacent grains, and secondary recrystallisation, where grains grew into their neighbours which were apparently in equilibrium with them.

Dr. E. OROWAN explained that he had used the term secondary recrystallisation for two reasons. In the first place, it was that used by the discoverer twenty-eight years ago, and secondly, as they had come to regard grain growth as the result of a tendency to minimise the total surface energy of the material, use of such terms as abnormal grain growth involved putting a hypothesis into the name.

The influence of impurities had been shown by the inability of the authors to cause secondary recrystallisation in pure aluminium. The effect of impurities was considerable, but he did not think that it could be said that the impurity effect formed a basis for a hypothesis of secondary recrystallisation.

He agreed, with Dr. Cook that, within what they called secondary recrystallisation, there were two different-looking phenomena, one producing acicular crystals and the other equiaxed ones and he thought there might be a tertiary recrystallisation.

In reply to Dr. Chaston, the factor of 1.15 came into the question of rolling because it did not matter whether, in straight rolling, spread were prevented by having side guides or by roll friction.

### Author's Reply

Dr. W. BOAS, in reply, said that the process was definitely not continuous with grain growth, which consisted in a general increase in grain size. In secondary recrystallisation, only some of the grains grew. He agreed with Dr. Orowan that the use of "abnormal grain growth" to describe the phenomenon involved an explanation.

He was not clear about the question of tungsten; as Dr. Pfeil had pointed out, powder metallurgical products might behave quite differently from normal metals. Dr. Boas agreed with Dr. Lepp that energy measurements were very important and, although they were carrying out experiments of that type at Melbourne, there were many associated difficulties.

He could not, from memory, answer Dr. Chaston's query about purity, but the straight and compression rolling tests were carried out on the same material and therefore comparable, but it might explain the difference of which Dr. Cook spoke. In reply to Dr. Cook, the large crystals

shown in one of the sheets were produced by cross-rolling. He wanted to emphasise the difference between cross-rolling and what they had termed compression rolling. Referring to Dr. Orowan's earlier remarks, Dr. Boas agreed that the yield stress was different in compression-rolling and the compression-rolled material always work-hardened more than the straight rolled material, but the grain size after primary recrystallisation was amazingly similar. He agreed with Dr. Orowan that inhomogeneity of rolling deformation was unlikely to affect their results on account of the thinness of the strips. Honeycombe and Collins, in America, had recently shown that the effect was less important in rolling than in drawing.

#### OBSERVATIONS ON THE ANNEALING CHARACTERISTICS OF AN ALUMINIUM-COPPER-MAGNESIUM ALLOY.

By MAURICE COOK, D.Sc., Ph.D., F.I.M. and  
T. L. RICHARDS, B.Sc., Ph.D., F.I.M.

**O**BSERVATIONS recorded in this paper were made in the course of a detailed study of the cold-working and annealing characteristics of a well-known type of commercial heat-treatable aluminium alloy, and the results serve to explain the salient and typical features of annealing curves of an alloy of this kind as well as to add to available evidence on the process of recovery and recrystallisation.

The material used was all from the same original casting, and stock at a thickness of 1 in. was hot-rolled from a 5-in. thick extruded slab. For the various experiments, material from this stock was annealed for 2½ hr. at 380° C. and air-cooled, before cold rolling. The composition of the alloy was: copper 4.01, magnesium 0.68, manganese 0.55, silicon 0.36, iron 0.38%, traces of nickel chromium, titanium, lead, tin, and zinc, remainder aluminium.

The experimental work consisted essentially of hardness measurements and structural observations by X-ray and microscopic methods on materials rolled and annealed under a variety of conditions. Typical hardness and X-ray data resulting from the experiments are reproduced, but no photomicrographs are included, since results obtained by the X-ray methods were more relevant and conclusive.

Annealing curves of heat-treatable alloy, cold-rolled from annealed 1-in. thick hot-rolled stock with reductions in thickness ranging from 15 to 90%, all show a marked hardening before softening, which occurs in two well defined stages, and a final increase in hardness with increasing temperature above that required to obtain minimum hardness. The two successive steps in softening are due to the removal of lattice distortion or recovery, and to actual recrystallisation respectively. These observations provide additional evidence that softening of cold-worked metals on annealing is a two-stage process.

The final increase in hardness with increasing annealing temperature above that corresponding to minimum hardness, shown by all the annealing curves, is a result of copper and magnesium being taken into solution. As in other metals, increase in the magnitude of the cold-rolling reduction of the fully recrystallised alloy lowers the recrystallisation temperature.

Strip subjected to non-recrystallising anneals does not age-harden since it is not in a supersaturated state, but it is harder than material subjected to recrystallising anneals which is supersaturated and, therefore, age-

hardenable. On cold rolling, the former work-hardens at a much slower rate, and the difference in hardness after any given rolling reduction would appear to be equal to the extent to which the latter age-hardens in the unworked state. Recrystallised material age-hardens appreciably in the unworked condition, but the extent of age-hardening subsequent to cold rolling decreases to a constant value with increasing rolling reductions.

Annealing curves of strips which have been cold rolled with either recrystallising or non-recrystallising intermediate anneals show all the main features common to those of strip cold rolled from annealed hot-rolled stock, except that there is no increase in hardness before this initial softening in the curves of strip subjected to intermediate non-recrystallising anneals. It would, therefore, seem that the initial hardening observed in the annealing curves of strip is directly associated with ageing.

By increasing the number of non-recrystallising intermediate anneals, complete equilibrium condition in the material is progressively approached and the recrystallisation temperature lowered.

Cold rolling results in a progressive increase in the degree of preferred orientation of crystals, which is unaffected by subsequent non-recrystallising anneals, that is, heating under conditions which effect recovery only. Strip cold rolled with a sequence of small reductions and intermediate non-recrystallising anneals to a total reduction in thickness of 90% shows the same degree of preferred orientation as strip cold rolled with a single reduction of 90% without intermediate annealing.

On solution heat-treatment at 500° C., strip cold rolled with a final reduction of 25% after a recrystallising anneal, recrystallises with a completely random orientation of crystals, whereas material rolled with final reductions of 44 and 88% recrystallises with a preferred orientation similar to that present in the strip after cold rolling. Strip processed with a rolling reduction of 90% without intermediate annealing, or with a total reduction of 90% and intermediate non-recrystallising annealing, shows, after solution heat-treatment, a preferred orientation different in character from that in strip in the rolled condition, which indicates complete atomic re-arrangement, a fact clearly distinguishing recovery from recrystallisation.

#### Discussion

Dr. H. SUTTON said that it had been known for some time that worked metals could be softened at temperatures below those at which recrystallisation could be detected, and also that very pure metals in the cold worked state showed evidence of recrystallisation at quite low temperatures. For example, the authors had found recrystallisation effects absent, even at 280° C, whereas Hutchinson had found that aluminium of high purity, cold worked slightly at liquid-air temperatures, showed line broadening and hardening at normal temperatures, whilst the very high purity aluminium did not show those effects. In other words, that material was self-annealing at room temperature. The changes occurring in the lower range of annealing temperature were interesting. Niemann and Stevenson found that that component of internal friction introduced by cold work in  $\alpha$ -brass, was removed by annealing at a temperature far below the recrystallisation temperature.

It was clear that, for materials whose basis was aluminium, which could be made to recrystallise or show substantial grain growth at normal temperatures when in a high



state of purity, the elements added in a commercial alloy must have a powerful effect. Bassey and Booth attributed it to copper aluminide particles, and made a case for controlling grain growth, in that class of alloy, by precipitating copper aluminide in particular conditions. He believed that the manganese-aluminium constituent was also of importance.

Sheet aluminium had often to be worked, by bending or flanging, before service, and the effect of overstrain was to change the proof stress. Tensile overstrain would increase the tensile proof stress and lower the compressive proof stress. Such information as was available suggested that quite low temperature annealing would remove the effect and he wondered whether the authors had any comments to make on the subject.

PROF. A. VON ZEERLEDER (Switzerland) said that in the last few years the Swiss aluminium industry had changed to continuous casting for rolling slabs. Previously, on low temperature annealing (slightly below 275° C) and deep drawing, the earing produced, due to preferred orientations, had been along and across the direction of rolling. Last year, 80% of the samples checked showed the preferred orientations to be at 45° to the direction of rolling.

Professor von Zeerleder said they had repeated the authors' experiments on pure aluminium and on Al-Cu-Mg alloy and had obtained similar results, although the temperature at which the effects occurred varied slightly with the alloy. They did not find the slight increase of hardness below 150° C and he wondered whether it was a special effect of the Al-Cu-Mg alloy, or whether it was not observed consistently—it was a point worthy of investigation.

MAJOR P. C. VARLEY thought it was unfortunate that an age-hardening alloy had been chosen, as it was difficult to separate the age-hardening phenomena from those of recovery and recrystallisation. He found that he was at variance with the authors on the interpretation of some of the results. They ascribed the increase in definition of the X-ray diffraction rings, in the early stages, to recovery. He had been unable to detect it in pure aluminium or a simple binary alloy. Spillet had shown that with a cold-rolled piece of aluminium of fairly coarse grain size, the X-ray pattern showed blurred spots, and did not change in any way until new sharp spots appeared as a result of new crystals being formed. It seemed more probable that the sharpening of the X-ray ring pattern during annealing, and the difference in sharpness between the metal rolled with a recrystallising or non-recrystallising anneal, were due to local lattice distortions due to the presence of copper and magnesium atoms in the solid solution.

Although it appeared, at first sight, that the peculiar step, at 280° C, in the isochronal annealing curves, ascribed to the change from recovery to recrystallisation, might be due to some form of age-hardening, he had not been able to account for it on those lines. Unlike Professor von Zeerleder, he had never been able to find it with pure aluminium. The only way in which he could get such a step involved two unjustifiable assumptions: (1) That the age-hardening maximum occurred at 300° C instead of 250° C, which was unlikely, and (2) that the recrystallisation of the aluminium matrix was complete before the step occurred, which the authors had shown was not the case. He had found that, for pure aluminium and simple binary alloys, recovery and recrystallisation merge one into the other without detectable discontinuity but, with an alloy similar to the authors', he found the step.

An explanation of the effect of intermediate anneals on the recrystallisation temperature for commercial

purity aluminium could be based on the varying amount of silicon in solid solution, but he was not entirely satisfied that that was the whole story.

MR. R. W. CAHN said that he believed there was a good deal of evidence for a process of recovery prior to new grains appearing. It was interesting to note that the amount of recovery increased as the original hardness, due to working, increased. The resistivity of pure aluminium had been measured as a fraction of the time of anneal at various temperatures, and it was found that it decreased to a limiting value, which was not the value for recrystallised material. A Russian worker carried out experiments on the effect of recovery on subsequent recrystallisation and found that the number of grains obtained with deformed polycrystalline aluminium decreased as the recovery annealing time increased, but it decreased to a limit.

Mr. Cahn had done some experiments on bi-crystals of aluminium with a grain boundary down the middle. Marks were made across and at high temperatures they were stressed in shear. They were removed at intervals and the displacement measured. It proved that the rate of creep the decrease became almost zero after a while and that the limiting amount of creep increased as the stress increased.

He suggested that in the alloy the authors had studied there was a certain amount of very slight creep of that sort at the grain boundaries. There was a good deal of evidence in the literature that a large proportion of the deformation in polycrystalline metals was concentrated near the grain boundaries, and a slight motion of the grain boundary, which might not be seen microscopically, would be sufficient to cause a considerable decrease in accumulated stresses near the boundary. The hardness would not fall to the value for recrystallised material, as when the stress near the boundary fell it would be unable to cause further motion.

DR. T. LI. RICHARDS, in reply, said that the note of Hutchinson, which Dr. Sutton had suggested presented evidence of self-annealing, could be interpreted as presenting evidence of recovery. He agreed with Major Varley that the material was not ideal, but the results presented were the part of the work, which they had had to do on such an alloy, which they felt would interest members of the Institute. With super-pure aluminium he believed the resolution of diffused rings would not be found because, he thought, recovery was so rapid at room temperature. It was only possible to produce stable distortions in super-pure aluminium at low temperatures.

He appreciated Professor von Zeerleder's question about the initial hump; they were not really satisfied with the explanation. With pure metals it was very small, in solid solution alloys, such as 70/30 brass, it was quite considerable. One had to appreciate the effect of small amounts of impurities. Suppose one had 0.1% of a foreign element in a metal, then, with uniform distribution, every tenth atom in whichever direction one moved could be a foreign atom. If, therefore, one had discontinuities in the crystal the foreign atoms would not have far to migrate. In the strain-ageing of mild steel, carbon caused lattice distortion, and on ageing, even at room temperature, the carbon diffused into the dislocations and caused an increase in hardness.

Dr. Richards was surprised that Major Varley had been unable to observe the two distinct steps because they were clearly separated on their curves and Professor von Zeerleder had also found them.

He said they would examine Mr. Cahn's suggested explanation with great interest.

# The Potentialities of Aluminium and its Alloys for the Paper-making Industry

*Some suggestions for possible applications of aluminium and aluminium alloys in the paper-making industry were made by Mr. F. W. Rogers in a paper he presented at a recent meeting of the Technical Section, Northern Division, of The Paper Makers Association of Great Britain and Ireland, some interesting aspects of which are discussed in this article.*

**A**LTHOUGH the aluminium industry in this country concentrated practically the whole of its output, for so many years, on the manufacture of war materials and components, the change from war to peace has been effected with remarkable success. Not only have aluminium and its alloys reclaimed the applications in those fields in which they proved their usefulness and adaptability before the war, but they have been applied with increasing success in new fields. In addition to road, rail, air, and sea transport; electrical apparatus; food preparation and handling equipment; mining appliances; and in many forms of general engineering; aluminium and its alloys have proved of immense value in helping in the solution of the urgent housing problem.

Success in such contrasting fields as aircraft engineering and domestic building show the versatility of this material and support the claims made for it when it is properly selected and applied. As in the case of other industries, the application of aluminium to the paper-making industry has been retarded temporarily for various reasons, many of which were mentioned by Mr. Rogers. But it may be that, while many industries have benefited from war-time experience in the fabrication and use of aluminium alloys, the paper-making industry has not been so fortunate and to increase the use of suitable alloys would incur those teething troubles usually associated with the use of unfamiliar materials. Undoubtedly opportunities exist in this important industry for the greater use of aluminium and Mr. Rogers suggested developments on the basis of close co-operation between the papermaking industry, the paper-making machine maker and the Aluminium Development Association, which he represented, would be to their mutual advantage.

The chief purpose of the paper was to indicate the potentialities of aluminium and aluminium alloys, and with this object Mr. Rogers described many of the properties and characteristics of these materials, in order to indicate the need for selection according to the conditions of service. He discussed pure aluminium, heat-treatable and non-heat-treatable alloys and referred to their durability and to their resistance to corrosion from attack by many corrosive media, and the forms in which they were available—as sand, gravity- or die-castings; forgings; extruded sections; plate, sheet and strip; rolled bar and rod, tube, wire and rivets.

Fabrication methods developed in working the materials were discussed, particularly machining, cold forming, welding, riveting, brazing and soldering. The surface finishing of aluminium and its alloys was also briefly reviewed, and then some typical examples were given of applications in familiar fields in an effort to indicate possible uses of these materials in the paper-making industry and to provoke suggestions from within the industry.

Some information, directly applicable to the industry, but of a general character, was given of the uses of these materials in the production of pulp and paper. Mention was made of aluminium alloy logging racks used in Canada to reduce wooden sleigh weights. Logging sleighs completely in aluminium have been designed with the object of saving about 50% in weight by comparison with the wooden sleigh. Portable log chutes form another application in which saving in weight of the chute itself is the chief attraction. The first known Canadian application of aluminium to log flumes is dated June, 1945, and the results are described as most attractive. There is a particular reason for this—apart, that is, from the economy in erection and saving in maintenance. This is that the patrol crew, normally required to prevent the jamming of logs in the timber flume, has much less work to do with the aluminium flume; the smoothness and slight greasiness of the aluminium surface gives a freer run. It has been claimed that a worthwhile reduction in weight has been gained by the use of aluminium haul-up chain lugs.

Logging skidways are being made with the frames of forged aluminium, but no results of experience with these are yet to hand. Extruded sections in aluminium alloy are in use for the frames of portable tree-cutting saws. Aluminium tube of 1½ in. diameter is used for the handles of pike poles. These have the advantage that they float and, although stronger than wooden handled poles, weigh less—the actual weight of the aluminium-handled pole is 3 lb.

A fairly common use of aluminium sheet in the paper-mill is for paper-machine hoods. A maximum size of hood given by a Swedish manufacturer is: length 66 ft., breadth 16 ft. 6 in., and height 13 ft., but other sources refer to aluminium hoods of lengths from 100 ft. to 200 ft. Another application from Scandinavia is the use of aluminium alloy for screens. Some years ago some consideration was given to the project in this country but no development has yet been reported.

Table rolls are supplied in diameters up to 12 in.; also castings for table roll heads. Attempts to use bare aluminium baffle plates between table rolls are reported as not very successful due to corrosion by the pulp, presumably by the inclusions of aluminium sulphate and of chlorine in bleaching chemicals. A core winder shaft in aluminium alloy will obviously save dead weight and make for easier changes: a saving of 150 lb. on a winder shaft 22 ft. long is reported. Aluminium roller guides have been used successfully, but not apparently to a very great extent.

It has been suggested that the value of light metals in the paper-making industry lies chiefly in their application to auxiliaries such as sizing troughs, colour tubs, drying racks and storage tanks, and less to parts of larger units such as making machines and calenders. Certainly, if the auxiliaries endure comparatively more

wear and tear, contact with damp, steamy atmosphere and chemicals, and more handling by unskilled workers they may form the more attractive technical problem. On the other hand, when considering possibilities for investigation, it is worth remembering that inaccessible, unwieldy components are those for which a long life is particularly attractive.

Between these extremes, however, there would appear to be opportunities for a light, strong and durable material in coating machines: for example, the trough, the roller or rollers carrying the felt; the roller driving gear; brushes, brush supports and crank mechanism. Gear covers and other shields, either cast or fabricated from sheet alloy, form additional possibilities. The use of aluminium for main machine castings is also worth serious consideration, bearing in mind, firstly, that light weight may have considerable advantage in handling—especially in the replacement of large components in difficult places; secondly, the effect of lower machining costs with aluminium where sufficient machining is required to make this an important factor.

Although Mr. Rogers gave more attention to the aluminium-base materials available, their properties, forms and methods of treatment, manipulation, joining and surface finishing, which lead to a sound basis for the selection of material, according to requirements of

strength, durability and the operations necessary in producing or forming a component, he found an appreciative audience, and the subsequent discussion proved both interesting and informative. Many suggestions were made by experts in the industry, and Mr. Rogers would be able to report some ideas likely to develop, as a result of investigation and experiment, with advantage to the industry; success, however, will depend largely upon the degree of co-operation fostered between the paper-making and aluminium-producing industries.

### Gas Welds in a High Strength Aluminium Zinc-Magnesium Copper Alloy\*

THIS Report, by J. Pendleton, B.Eng., A.I.M., describes work carried out at the British Non-Ferrous Metals Research Association's laboratories for the Committee on "Development of Strong Aluminium Alloys for Welding" of the British Welding Research Association.

The development of high strength materials based on the aluminium-zinc-magnesium-copper series of alloys has called for investigation into the welding characteristics of this type of alloy. This report describes a general investigation on a typical alloy in which joints were made by oxy-acetylene welding.

The welds were made in 18, 14 and 10 S.W.G. sheets of an alloy containing: zinc, 5.5%, magnesium, 2.8%, and copper, 0.5%, using filler rods of the same composition. The welds were examined mainly by tensile tests and hardness explorations.

Cracking of welds made under constraint was experienced, as well as porosity of the overheated metal adjacent to a weld, which may be accompanied by superficial blistering on the underside of the sheets. The mechanism responsible for this porosity and blistering is possibly analogous to that of similar defects found in gas welds in aluminium-magnesium alloys.

### Further Investigations on the Pressure Welding of Light Alloy Sheet\*

THIS is the second of a series of Reports on the welding of light alloys at temperatures below their melting points, and, besides dealing further with the work that has been carried out on the more readily weldable alloys down to room temperature, describes the attempts that have been made to improve the strengths of welds in less weldable alloys. Work has been done on the effect of the oxidation of the specially prepared material prior to welding, and corrosion tests have been carried out on welded joints in two media.

In the section of the Report on the potential applications of the process—perhaps the most important part of the work—details are given of some specific applications of the process, including pressure welding by means of the conventional projection welder and the making of a lapped seam by means of cold welding.

Reproduction of photomicrographs of welds in aluminium-clad duralumin and aluminium-magnesium-silicon alloy clad duralumin, both before and after heat-treatment, of welds made between aluminium and magnesium, and of cold pressure welded seams in high purity aluminium are included.

\* The complete Report is published in the October, 1948, issue of the Welding Research Supplement to the Transactions of the Institute of Welding.



Camera crane casting in "Hiduminium" RR. 50; 8 ft. long, 21 in. wide  $\times$  16 in. deep at one end, tapering to 15½ in. wide  $\times$  6½ in. deep, with two legs 6 in. wide  $\times$  3 in. deep, and wall thickness ½ in. Weight 230 lbs. Cast by High Duty Alloys, Ltd., for D. & P. Studios, Ltd., Denham.



# The Determination of Copper in Carbon and Low-Alloy Steels\*

Report of the Methods of Analysis Committee of the Metallurgy (General)  
Division of the British Iron and Steel Research Association.

*A critical examination has been made of existing methods for the determination of copper in low-alloy steels, and as a result a method has been recommended to the British Standards Institution for publication as a standard method. The principle involved depends upon a sulphide separation of the copper, ignition, and solution in nitric/sulphuric acids, followed by iodometric titration.*

## Introduction

TOWARDS the end of its term of office the Standard Methods of Analysis Sub-Committee<sup>1</sup> was asked by one or two members if it would formulate a standard method for the determination of copper in low-alloy steels. The firms concerned were experiencing difficulties with certain classes of steel and, as the presence of copper was suspected to be the source of the trouble, the need for a reliable method for its determination became necessary.

A draft method was put forward which involved the separation of copper as sulphide from a sulphuric-acid solution, using sodium thiosulphate. The sulphide was then ignited, dissolved in nitric acid, and following the removal of any iron or silica present, the iodometric titration was carried out in the usual way. The presence of molybdenum or vanadium caused interference which was overcome by a caustic soda separation after the solution in nitric acid. The cupric hydroxide was filtered off and, after ignition, redissolved in nitric acid and the procedure continued. This method gave satisfactory results as shown by Table I, but certain modifications were suggested including additions of urea, ammonium thiocyanate, and sodium fluoride. The revised method<sup>2</sup> had not been submitted to an extensive trial when the responsibilities of the Committee were taken over by the Methods of Analysis Committee of B.I.S.R.A. The few comments that had been made had raised certain objections to the revised titration procedure.

## Preliminary Investigation

As the determination of copper in low-alloy steels came within the terms of reference of the Pig Iron, Carbon and Low-Alloyed Steels Sub-Committee,<sup>3</sup> the revised method was handed to that Sub-Committee for examination. The procedure for separation of the copper

as sulphide was approved and also the procedure for removal of molybdenum or vanadium.

A preliminary series of tests was carried out to confirm, or otherwise, the points raised before the revised method was passed to B.I.S.R.A. With regard to the solution of the ignited precipitate some difficulty was experienced in obtaining complete solution in the suggested 5 ml. of nitric acid (sp. gr. 1.2), but complete solution was readily obtained in 5 ml. of nitric acid (sp. gr. 1.42). On addition of the potassium-iodide solution to the copper solution the development of the iodine colour was slow and obviously incomplete, as, in the subsequent titration, after removal of free iodine from the solution with sodium thiosulphate more iodine was liberated on standing. If the titration was completed very slowly, allowing the liberation of iodine to proceed after each small addition of sodium-thiosulphate solution, then a more or less correct titration value was obtained, although the end-point was rather uncertain. When tests were carried out using increased amounts of potassium iodide the liberation of iodine was instantaneous, but the lagging effect of the end-point was accentuated. The addition of a thiocyanate to liberate any iodine occluded by the starch iodide was a decided advantage and improved the end-point considerably, removing the lagging effect which had been obtained previously. Potassium thiocyanate was found to be more suitable than the ammonium salt, as the latter was very difficult to obtain in a pure enough form, and some members reported that there was a definite destruction of iodine on the addition of the ammonium thiocyanate. The addition of sodium fluoride to prevent the interference of iron in the titration was satisfactory, but the addition of urea for suppression of any nitrous acid was considered to be unnecessary.

After consideration of the preliminary tests it was felt that the troubles experienced were perhaps largely due to the volume of the solution before titration (70/80 ml.) particularly the slow liberation of iodine and the lagging effect. It is generally acknowledged that a copper titration of this type is more satisfactory when performed in the smallest possible volume of solution.

\* Paper MG/D/172/48 submitted by the Methods of Analysis Committee of the Metallurgy Division of the British Iron and Steel Research Association, received September, 1958.

<sup>1</sup> The Standard Methods of Analysis Sub-Committee of the Heterogeneity of Steel Ingots Committee, Iron and Steel Institute.

<sup>2</sup> See Appendix I.

<sup>3</sup> See Appendix II.

TABLE I.—RESULTS OBTAINED BY THE ORIGINAL DRAFT METHOD ON STEELS CONTAINING APPROXIMATELY 0.4% MOLYBDENUM

Steel	Analyst																Using Other Methods			
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
1. . . . .	0.120	0.120	0.123	0.126	0.118	0.115	0.122	0.127	0.120	0.120	0.115	0.123	0.116	0.125	0.122	0.124	0.123	0.120	0.124	0.109
2. . . . .	0.190	0.195	0.194	0.197	0.191	0.190	0.192	0.196	0.190	0.188	0.195	0.193	0.185	0.200	0.199	0.184	0.190	0.193	0.197	0.172
3. . . . .	0.230	0.230	0.232	0.231	0.231	0.240	0.236	0.241	0.240	0.248	0.247	0.251	0.242	0.258	0.255	0.232	0.243	0.240	0.248	0.226
4. . . . .	0.730	0.800	0.779	0.788	0.777	0.773	0.769	0.781	0.770	0.788	0.779	0.781	0.777	0.782	0.784	0.756	0.780	0.776	0.779	0.760
5. . . . .	0.120	0.105	0.104	0.110	0.091	0.105	0.094	0.108	0.100	0.105	—	0.111	0.100	0.106	0.112	0.110	0.110	0.090	0.106	0.091

## Investigation of the Titration Procedure

In order to find the optimum conditions for titration the recommended method for precipitation of the copper sulphide was used and the four following procedures for the solution of the ignited precipitate and subsequent titration were put forward for trial and comment:—

(i) Following ignition, dissolve the precipitate in 5 ml. of nitric acid (sp. gr. 1.42) and evaporate to low volume (1 ml., just short of dryness). Cool and dilute with 10 ml. of water.

Add 0.5 g. of sodium fluoride, and when dissolved make the solution alkaline with ammonium hydroxide (1 : 1) until the blue ammine colour is fully developed. Cool, acidify with dilute acetic acid to an excess of 1 ml. and again cool. Add 5 ml. of potassium-iodide solution (40%) and titrate the liberated iodine with standard sodium-thiosulphate solution until the brown colour is almost discharged. Add 2 ml. of starch solution, 10 ml. of potassium-thiocyanate solution and titrate until the blue colour is discharged (leaving a white precipitate at the end-point).

(ii) Following ignition, dissolve the precipitate in 5 ml. of nitric acid (sp. gr. 1.42), add 2 ml. of sulphuric acid (1 : 1) and evaporate just to fumes of sulphur trioxide. Cool, dilute with 10 ml. of water.

Complete the titration as described in para. 2 of (i) above.

(iii) Following ignition, fuse the precipitate with 0.5 g. of potassium bisulphate. Cool, dissolve the melt in water and adjust the volume to 10 ml.

Complete the titration as in (i) above.

(iv) In this procedure the precipitate is taken *before* ignition.

Transfer the paper and precipitate to a 125-ml. conical beaker, add 20 ml. of nitric acid (sp. gr. 1.42) then add 5 ml. of perchloric acid (sp. gr. 1.54) and evaporate to fumes. Fume for 3 minutes, cool, and dilute with 10 ml. of water.

Complete the titration as in (i) above.

The solutions used in these tests are the same as in Appendix III.

The results obtained from these four procedures are shown in Table II.

TABLE II.—RESULTS OBTAINED USING DIFFERENT PROCEDURES ON A BASIC OPEN-HEARTH STEEL CONTAINING APPROXIMATELY 0.25% COPPER

Procedure	Analyst								
	A	B	C	D	E	F	G	H	I
I .. ..	0.233	0.242	0.250	0.233	0.238	0.238	0.244	0.245	0.248
II .. ..	0.237	0.248	0.250	0.234	0.238	0.235	0.244	0.245	0.248
III .. ..	0.232	0.235	0.240	0.232	0.240	0.239	0.240	0.240	0.248
IV .. ..	0.236	0.246	0.250	0.236	0.243*	0.241	0.244	0.251	0.249

\*  $\pm 0.012$ —other results all within  $\pm 0.003$ .

## Conclusions

All four procedures gave good results, but several points were raised in discussion.

In procedure (iv) the time and degree of fuming of the perchloric-acid solution is critical, as it is essential that all sulphur present should be completely oxidised, otherwise some copper will be in the cuprous state and fail to react with potassium iodide.

The effect of variation of this fuming time is shown in Table III.

TABLE III.—EFFECT OF FUMING TIME IN PROCEDURE (IV)—RESULTS OBTAINED ON STANDARD STEEL CONTAINING 0.48% COPPER

Series	First appearance of fumes		1 min. fuming		3 min. fuming		5 min. fuming		5 min. fuming and 20 min. digestion	
1 ..	nil	0.36	0.44	0.42	0.46	0.44	0.47	0.48	—	—
2 ..	0.44	nil	0.45	0.41	0.44	0.46	0.46	0.48	0.48	0.48
3 ..	0.41	no end-point	0.45	0.42	0.46	0.47	—	—	0.48	0.48

Using procedure (II), this sample gave  $0.48 \pm 0.002\%$  on five tests.

When perchloric acid had been used, it was found that the end-point was perfectly satisfactory without the addition of potassium thiocyanate, the only unusual feature being the formation of a heavy precipitate of potassium perchlorate.

Procedure (iii) although ensuring complete solution of the ignited precipitate tended to give a slightly recurring end-point, and so it was decided that (i) or (ii) should be used in the final draft.

Procedure (ii) was finally decided on, where the use of a definite quantity of sulphuric acid ensured that in all tests the concentration of salts in solution would be the same, and this was found to be an advantage over (i), where the evaporation of nitric acid to 1 ml. cannot be so judged. Two recommendations were made for slight alteration of the titration conditions, that the quantity of potassium iodide should be increased to 5 ml. of 60% solution and that instead of acidifying with dilute acetic acid, glacial acetic acid should be used.

TABLE IV.—RESULTS OBTAINED USING THE RECOMMENDED METHOD FOR THE DETERMINATION OF COPPER

Steel Type	Analyst									
	A	B	C	D	E	F	G	H	I	J
1% Cu, 0.5% Mo	0.779	0.776	0.775	0.764	0.781	0.776	0.778	0.770	0.784	0.776
0.25% Cu R.O.H.	0.247	0.246	0.246	0.240	0.250	0.242	0.244	0.243	0.247	0.244
0.05% Cu B.O.H.	0.042	0.044	0.044	0.041	0.045	0.045	0.042	0.041	0.044	0.042

These recommendations were adopted and using the revised method<sup>4</sup> on three circulated steel samples, members of the Sub-Committee reported the results shown in Table IV. Following this, the method was finally approved and was accepted by the main Committee for submission to the B.S.I. as a standard method.

<sup>4</sup> See Appendix III.

## APPENDIX I

Draft Volumetric Method for the Determination of Copper in Carbon and Low-Alloyed Steels.

### Solutions Required

**Dilute sulphuric acid (1 : 6).**—To 1 litre of cold water, add cautiously 300 ml. of sulphuric acid (sp. gr. 1.84) and dilute to 2 litres.

**Dilute acetic acid.**—Dilute 350 ml. of glacial acetic acid to 1 litre.

**Potassium Iodide (40%).**—Dissolve 40 g. of pure potassium iodide in water and dilute to 100 ml.

**Standard sodium thiosulphate.**—Dissolve 4 g. of sodium-thiosulphate crystals in 1 litre of water, containing 0.1 g. of sodium carbonate (A.R.). Standardise the solution as follows:—

Dissolve 0.05 g. of pure electrolytic copper in 5 ml. of nitric acid (sp. gr. 1.20) in a 150-ml. conical beaker and boil gently to remove brown fumes. Add 40 ml.

of water, made just alkaline by addition of ammonium hydroxide (sp. gr. 0.880), cool and then acidify with dilute acetic acid to an excess of 5 ml. Cool, add potassium iodide and titrate with the thiosulphate solution as described in the method below.

### Procedure

Transfer 10 g.<sup>1</sup> of the sample to a 600-ml. conical beaker and dissolve in 100 ml. of dilute sulphuric acid (1 : 6). Dilute to 350 ml. and heat to boiling, add cautiously 10 g. of sodium thiosulphate [or 25 ml. of sodium thiosulphate solution (40%)] and boil for 10 minutes (until the precipitate settles rapidly). Filter through a Whatman No. 540 filter paper, 12.5 cm., washing well with warm water containing a little hydrogen sulphide. Dry and ignite the paper and precipitate in a porcelain or silica crucible at 550°C. maximum until carbonaceous matter is destroyed.

Cool, transfer the ignited precipitate to a 100-ml. beaker and dissolve in 5 ml. of nitric acid (sp. gr. 1.20).<sup>2</sup> Dilute to 30 ml. with water, warm and add ammonium hydroxide (sp. gr. 0.880) in slight excess. Digest for 2-3 minutes and filter through a Whatman No. 40 filter paper, 9 cm., washing with hot water. Dissolve the precipitate through the filter with 3-4 ml. of nitric acid (sp. gr. 1.20) and, after diluting to 30 ml. with warm water, reprecipitate with ammonium hydroxide, filtering and washing as above.

Evaporate the combined filtrates to about 5 ml. and add ammonium hydroxide (sp. gr. 0.880) until the solution just reacts alkaline to litmus or until the blue ammine colour is developed. Cool, acidify slightly with dilute acetic acid, followed by 5 ml. in excess and again cool. Add 5 ml. of potassium-iodide solution (40%) and titrate the liberated iodine with a standard sodium-thiosulphate solution. When the brown iodine colour is almost discharged, add 2 ml. of starch solution (1%) and continue the titration until the blue colour changes to a yellowish white which persists for 20 seconds.

$$\text{Copper \%} = \frac{\text{ml. of sodium-thiosulphate solution}}{\text{Weight of sample}} \times 0.1 \text{ (approx)}$$

Weight of sample

<sup>1</sup> For copper contents greater than 0.10% use 5 g. of sample.  
<sup>2</sup> If the sample contains more than 0.25% of molybdenum, add sodium-hydroxide solution (5%) to an excess of 2 ml. Boil for 3 minutes, allow to settle and filter on a Whatman No. 540 filter paper, 12.5 cm., washing with sodium-hydroxide solution (0.5%). Dissolve the precipitate in 10 ml. of nitric acid (sp. gr. 1.20), washing with hot water. Evaporate the solution to 3 ml., dilute to 30 ml., and proceed with the ammonia precipitation.

### APPENDIX II

Constitution of the Pig Iron, Carbon and Low-Alloyed Steels Sub-Committee of the Methods of Analysis Committee, Metallurgy Division, B.I.S.R.A., at September 30th, 1947.

Mr. J. H. Wright (Chairman), Dorman Long & Co., Ltd.

Mr. O. Beadle, Cargo Fleet Iron Co., Ltd.

Mr. W. F. Charteris, Colvilles, Ltd.

Mr. S. W. Craven, I.C.I., Ltd. (Alkali Division).

Mr. J. M. Harrison, Lancashire Steel Corporation, Ltd.

Mr. J. D. Hill, Bragg Laboratory.

Mr. B. W. Methley, Steel Peech & Tozer, Ltd.

Mr. H. R. Pepper (Vice-Chairman), Stewarts & Lloyds, Ltd.

Mr. N. D. Ridsdale, Bureau of Analysed Samples, Ltd.

Mr. H. Thomas, Richard Thomas & Baldwins, Ltd.

Mr. W. Westwood, British Cast Iron Research Association.

### APPENDIX III

The Determination of Copper in Carbon and Low-Alloy Steels. (B.S. 1121, Part....).

#### (1) Introduction

(a) *Principle*.—Copper is precipitated as the sulphide from a sulphuric-acid solution of the steel by addition of sodium thiosulphate. This is filtered off, ignited, redissolved in nitric-sulphuric acid and the equivalent iodine, liberated by the addition of potassium iodide, is titrated with standardised sodium-thiosulphate solution.

(b) *Range*.—Up to 1.0% copper.

(c) *Reproducibility*.

With 0.05% copper present,  $\pm 0.003\%$  copper

„ 0.25% „ „  $\pm 0.006\%$  „

„ 1.0% „ „  $\pm 0.01\%$  „

(d) This method is not applicable in the presence of tungsten.

#### (2) Special Apparatus Required

Grade A graduated glassware shall be used throughout.

#### (3) Reagents Required

(a) All reagents shall be of guaranteed purity, and distilled water shall be used throughout. Solutions shall be freshly prepared and, where necessary, filtered.

(b) *Solutions*.

*Dilute sulphuric acid* (3 : 17).—To 800 ml. of cold water, add cautiously 150 ml. of sulphuric acid (sp. gr. 1.84), cool and dilute to 1 litre.

*Potassium iodide solution* (60%).—Dissolve 60 g. of pure potassium iodide in water and dilute to 100 ml.

*Potassium thiocyanate* (20%).—Dissolve 20 g. of pure potassium thiocyanate in water and dilute to 100 ml.

*Starch* (1%).—Stir 1 g. of soluble starch to a paste with 5 ml. of water, add 100 ml. of boiling water, and cool.

*Standard sodium thiosulphate*.—Dissolve 4 g. of sodium-thiosulphate crystals ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in water, containing 0.1 g. of sodium carbonate, and dilute to exactly 1 litre. 1 ml. of this solution is approximately equivalent to 0.001 g. of copper.

*Standard copper nitrate*.—Dissolve 1 g. pure copper in 10-ml. of water + 5-ml. of nitric acid (sp. gr. 1.42), boil off nitrous fumes, cool and dilute to exactly 1 litre.

#### (4) Sampling

Recommended methods of obtaining a suitable sample for the analytical procedure outlined below are described in B.S.....(in preparation).

#### (5) Procedure

Transfer 10 g.<sup>1</sup> (Note 1) of the sample to a 600-ml. conical beaker and dissolve in 100 ml. of dilute sulphuric acid (3 : 17). Dilute to 350 ml. and heat to boiling, add cautiously 10 g. of sodium thiosulphate (or 25 ml. of sodium-thiosulphate solution (40%)), and boil for 10 minutes (until the precipitate settles rapidly). Filter through a Whatman No. 540 filter paper, 12.5 cm.,

<sup>1</sup> For copper contents greater than 0.25% use 5 g. of sample.  
For copper contents greater than 0.50% use 2 g. of sample.



washing well with warm water containing a little hydrogen sulphide. Dry and ignite the paper and precipitate in a porcelain or silica crucible at a temperature not exceeding 550°C., until carbonaceous matter is destroyed.

Cool, transfer the ignited precipitate to a 125-ml. conical beaker, dissolve in 5-ml. nitric acid (sp. gr. 1.42)<sup>2</sup> (Note 2), add 10-ml. sulphuric acid (3 : 17) and evaporate just to fumes of sulphur trioxide. Cool and dilute with 10-ml. water.

Add 0.5 g. sodium fluoride and when dissolved make the solution alkaline with ammonium hydroxide (1 : 1) until the blue colour of the cuprammonium complex is fully developed. Cool, acidify with glacial acetic acid to an excess of 1 ml. and again cool. Add 5-ml. potassium-iodide solution (60%) and titrate the liberated iodine with standard sodium-thiosulphate solution until the brown colour is almost discharged. Add 2 ml. of starch solution, 10 ml. of potassium-thiocyanate solution

<sup>2</sup> If the sample contains more than 0.25% of molybdenum or vanadium, add sodium-hydroxide solution (5%) to an excess of 2 ml. Boil for 3 minutes, allow to settle and filter on a Whatman No. 540 filter paper 12.5 cm., washing with sodium-hydroxide solution (0.5%) and finally with hot water. Ignite as before and continue with the "Procedure."

## Staff Changes and Appointments

MR. F. M. DAVIES, L.I.M., has taken up an appointment as a metallurgical chemist at Swan, Hunter and Wigham Richardson, Ltd., Wallsend-on-Tyne.

DR. BRYNMOR JONES has been appointed a special director of the Whitehead Iron and Steel Company Limited, Newport, Mon.

MR. A. WOOD has been appointed foundry foreman with Deritend Precision Castings Ltd., Birmingham.

MR. J. H. HOBSON has been appointed general manager of F. Issels and Sons Ltd., Bulawayo, Southern Rhodesia, which recently became associated with John Brown and Company, Limited.

MR. ARNOLD LATHAM, production manager for the "Bristol" Brabazon project, has left the Bristol Aeroplane Company to take up an appointment with Metal Industries Ltd. He is succeeded by Mr. F. J. CHARD, production manager of the Experimental Dept. since 1945.

DR. H. ROXBEE COX, M.I.Mech.E., F.R.Ae.S., has been appointed chief scientist to the Ministry of Fuel and Power. He will work in close conjunction with the Scientific Advisory Council, which has also been appointed, and of which he is a member. The other members of the Council are: Eng. Vice-Admiral Sir Harold Brown, G.B.E., K.C.B., Chairman of the Fuel Research Board; Sir Charles Ellis, F.R.S., member of the National Coal Board; Professor Frederick H. Garner, O.B.E., Ph.D., Professor of Chemical Engineering, University of Birmingham; Sir Charles Goodeve, O.B.E., F.R.S., D.Sc., Director, British Iron and Steel Research Association; Dr. Ernest S. Grumell, C.B.E., D.Sc., M.I.Min.E., Chairman of the Fuel Efficiency Committee, Ministry of Fuel and Power; Mr. J. Hacking, M.I.E.E., Deputy Chairman of the British Electricity Authority; Dr. H. Hollings, D.Sc., F.R.I.C., Chairman of the Gas Research Board; Professor Dudley M. Newitt, M.C., D.Sc., Ph.D., F.R.S., Courtaulds Professor of Chemical Engineering, Imperial College of Science and Technology; Sir Harry Ricardo, F.R.S., Consulting Engineer and Technical Director of Ricardo and Co. Ltd.; and Professor S. Zuckerman, C.B., F.R.S., University of Birmingham.

(20%) and titrate until the blue colour is discharged, leaving a white precipitate at the end-point.

### (6) Standardisation

Measure 10 ml. of standard copper-nitrate solution ( $\equiv 0.01$  g. of copper) into a 125-ml. conical beaker, add 10-ml. sulphuric acid (3 : 17) and continue exactly as described in the "Procedure," Par. 2.

### (7) Calculation

(a) Let the amount of standard sodium-thiosulphate solution required for 0.01 g. of copper = A ml. Let the amount of standard sodium-thiosulphate solution required for copper in 10 g. of sample = B ml.

Then 1 ml. of standard sodium-thiosulphate solution  $\equiv 0.01/A$  g. of copper.

Then B ml. of standard sodium-thiosulphate solution  $\equiv 0.01B/A$  g. of copper.

= copper in 10 g. of sample.

or copper in sample =  $0.1B/A$  %.

(b) Results should be reported as percentage copper to two decimal places.

RUFERT H. MYERS, M.Sc., Ph.D., until recently Commonwealth Research Officer, The Baillieu Laboratory, University of Melbourne, has joined the staff of the Council for Scientific and Industrial Research and has become a member of the Atomic Energy team at Harwell.

MR. C. PARRY, MR. D. F. WALTON, MR. W. HALL and MR. H. H. MUMBY, have been appointed local directors of Messrs. Thos. W. Ward Ltd., Albion Works, Sheffield. Mr. Parry and Mr. Mumby have for many years been closely connected with this Company's shipbreaking activities, and Mr. Hall with scrap iron and steel, Mr. D. F. Walton is connected with the Company's activities as railway siding consultants and contractors, and is also a director of Darlington Railway Plant and Foundry Co. Ltd., one of the Ward group of Companies.

DR. M. A. VERNON, information officer of the Iron and Steel Institute, has joined the Science Department of the British Council in a similar capacity.

MR. P. E. GAINSBURG has joined the Development and Research Department of The Mond Nickel Company, Limited, as a research metallurgist.

MR. J. L. HARRISON, F.I.M., steel-plant manager at Catton and Company, Limited, has resigned to take up a similar appointment with Low Moor Alloy Steelworks, Limited, Bradford.

MR. J. A. PEACOCK, M.Inst.C.E., has been appointed chief engineer of Messrs. John Lysaght's Scunthorpe Works, Limited.

MR. W. EDGAR STANLEY has been elected a director of Darwins, Limited, Sheffield, and its associated companies.

MR. J. E. PRIESTLEY, A.Met., for nine years with Thomas Marshall and Co. (Loxley) Ltd., is taking up an appointment as production consultant to Messrs. McSkimming and Son Ltd., Dunedin, New Zealand.

MR. A. T. LEDGARD has been appointed blast furnace manager at the Redcar plant of Messrs. Dorman, Long and Co. Ltd.

MR. W. D. PUGH has succeeded Mr. F. Pickworth as managing director of the Darlington Forge Ltd. Mr. Pickworth will continue to hold office as Chairman of the Company.

# The Determination of Silicon and Manganese in Iron and Steel\*

Report of the Methods of Analysis Committee of the Metallurgy (General)  
Division of the British Iron and Steel Research Association

*Methods of analysis for silicon in plain and alloy steels and irons, excluding those containing major alloying contents of tungsten, or tungsten in association with molybdenum, and for manganese in all classes of iron and steel have been developed, and have been submitted as recommended standard procedures to the British Standards Institution. The silicon method is based on perchloric acid dehydration, and the manganese method on zinc oxide separation of the iron-chromium group and determination by ferrous sulphate and potassium dichromate titration following silver nitrate-ammonium persulphate oxidation. Various features of the methods are discussed, and typical results are given.*

## SILICON

THE object of the silicon investigation was to develop a tested and approved procedure of maximum applicability to the widest possible ranges of alloy compositions.

The work was carried out in the first instance by a Panel of the Standard Methods of Analysis Sub-Committee<sup>1</sup> and the results of their examination were further tested and confirmed by the Pig Iron, Carbon and Low-Alloyed Steels Analysis Sub-Committee and the Highly Alloyed Steels and Ferro-Alloys Analysis Sub-Committee.<sup>2</sup>

### Details of Investigation

A comparison of the efficiency of various mineral acids and their mixtures, as agents for dehydrating silicic acid to insoluble silica, indicated the marked superiority of perchloric acid. Dehydration by evaporation to a fumed perchloric acid concentrate was more complete in a single operation than with either sulphuric or hydrochloric acids, and in addition, the efficiency of perchloric acid as a decomposing agent for resistant carbides permitted a much wider application in connection with the rapid and effective decomposition of carbide bearing and highly alloyed steels in general.

Excellent results were obtained by the method (Appendix III), in which 50 ml. of perchloric acid is used for the dehydration of 5 g. test samples covering the range 0.4% silicon. Table I shows the results obtained on a wide range of plain and alloy steel compositions and further confirmatory evidence of the precision and range of the method is shown by the later work of the Sub-Committees (Table IV).

This method gives efficient decomposition of complex stable carbides in highly alloyed steels, yielding residues remarkably free from contamination. The dehydration efficiency was checked by making recoveries from filtrates and the results of many dozens of determinations, by different operators, indicated that an average amount of 0.006% remained in the filtrate from a single evaporation with a maximum recorded value of 0.012% (Table II).

TABLE I.—TYPICAL RESULTS OBTAINED BY THE SILICON-MANGANESE PANEL USING THEIR DRAFT METHOD FOR SILICON

Steel Type	% Silicon—Analyst					
	A	B	C	D	E	F
Plain carbon .. ..	0.28	0.28	0.28	0.30	0.28	0.28
4% Silicon .. ..	4.04	4.02	4.00	4.03	4.06	4.03
13% Chromium .. ..	0.33	0.34	0.32	0.33	0.33	0.33
Low Si, High S .. ..	0.007	0.010	—	0.005	0.007	0.006
25% Cr, 20% Ni .. ..	1.65	1.64	—	1.66	1.66	1.65
1½% C, 14% Cr, 3½% Co ..	0.45	0.44	—	0.46	0.45	0.45
18/8 + 1½% Ti .. ..	—	—	—	—	—	—
1% Al .. ..	0.06	0.08	—	0.07	0.07	0.06
BCS W2, 16% W .. ..	0.16	0.14	—	0.13	0.14	0.17
BCS 220, 7% W, 4% Mo .. ..	0.32	—	—	0.33	0.32	—
18/8 + 3% Mo .. ..	0.27	0.27	—	0.27	0.27	0.26
18/8 + 1½% Nb .. ..	0.65	0.65	—	0.64	0.65	0.65
14% Cr + 0.1% Zr + S ..	0.51	0.50	—	0.49	0.50	0.49

TABLE II.—RECOVERY OF SILICA FROM FILTRATES AFTER PERCHLORIC DEHYDRATION

Type of Steel	% Silicon	Grams SiO <sub>2</sub> recovered from filtrate (5 g. sample)
Plain carbon .. ..	0.285	0.0005
4% Silicon .. ..	4.03	0.0009
13% Chromium .. ..	0.33	0.0003
Low silicon, high sulphur ..	0.007	0.0001
25% Cr, 20% Ni .. ..	1.66	0.0007
1½% C, 14% Cr, 3½% Co ..	0.45	0.0008
18/8 + 1½% Ti + 1% Al .. ..	0.07	0.0010
BCS W2, 16% W .. ..	0.13	0.0007
BCS 220, 7% W, 4% Mo .. ..	0.32	0.0012
18/8 + 3% Mo .. ..	0.265	0.0005
18/8 + 1½% Nb .. ..	0.67	0.0006
14% Cr + 0.1% Zr + S .. ..	0.495	0.0007

Methods using much less perchloric acid—i.e., as little as 8 ml. per test have been examined, but the results have indicated that:—

- Incomplete carbide decomposition of highly complex steels occurs, resulting in greatly increased residue contamination.
- Dehydration to insoluble silica is less efficient in a single operation, up to 3 mg. being recovered by a repeat evaporation.
- There is extensive co-precipitation of titanium which is largely soluble when a high concentration of perchloric acid is present.

The results are valid for all classes of steel except high tungsten-molybdenum steels of the high-speed type. Very little titanium co-precipitates with the silica; this element is very soluble in solutions of high-perchlorate concentration, and silica residues obtained from steels containing as much as 1.5% titanium have shown

\* Paper MG/D/173/48 submitted by the Methods of Analysis Committee of the Metallurgy Division of the British Iron and Steel Research Association, received September, 1948.

1 Paper MG/D/7/46—Progress Report of the Silicon-Manganese Panel of the Standard Methods of Analysis Sub-Committee of the Heterogeneity of Steel Ingots Committee, Iron and Steel Institute, July, 1946.

2 Sub-Committees of the Methods of Analysis Committee, B.I.S.R.A.

negligible contamination. Zirconium, niobium, and tantalum contaminate the residue in substantial amounts, but accurate results are obtained by hydrofluoric acid treatment in the presence of sulphuric acid. Tungstic and molybdic acids also co-precipitate with silica and induce error by virtue of the volatility of their oxides at temperatures exceeding 800° and 550° C. respectively. This type of error is most marked on high molybdenum-tungsten high-speed steels.

Various methods of residue treatment have been examined with a view to extracting and removing tungstic and molybdic oxides from silica, but so far, no positive advance has been made. All methods adopted have resulted in partial re-solution of silica with consequent low results. The methods of residue treatment which have been examined include :—

- (a) Fusion of the residue with potassium bisulphate and extraction in citric, tartaric, oxalic acids and hydrogen peroxide.
- (b) Extractions in ammonia and in ammonium carbonate.

Details of these separation procedures are given in Table III.

TABLE III.—EXPERIMENTAL TREATMENTS FOR PURIFICATION OF SILICA PRECIPITATES CONTAINING TUNGSTIC AND MOLYBDIC OXIDES

Treatments 1-4 depend upon an initial fusion of the residue with  $\text{KHSO}_4$  prior to extraction: (i) Tests extracted direct; (ii) tests fused, and refluxed with 5 ml.  $\text{H}_2\text{SO}_4$  before extraction.

Treatment	16% W high speed steel (BCS 167)	7% W, 4% Mo high speed (BCS 220)	Remarks
1. Oxalic Acid Extraction in 100 ml. 5% oxalic acid.	(i) 0.08 (ii) 0.11	0.21 0.29	(i) extraction fairly clear. (ii) Tests made ammoniacal to dissolve tungstic acid and reacidified before filtration.
2. Tartaric Acid Extraction in 100 ml. of 10% tartaric acid.	(i) 0.08 (ii) 0.10	0.25 0.28	As above. Some reduction of Mo in BCS 220; blue precipitate colloidal on washing.
2. Hydrogen Peroxide Extraction in 100 ml. of $\text{H}_2\text{O}_2$ (10 vol.).	(i) 0.11 (ii) 0.10	0.28 0.29	As above. Some attack by $\text{H}_2\text{O}_2$ on filter.
4. Sulphuric Acid Extraction in 100 ml. of 5% $\text{H}_2\text{SO}_4$ .	(i) 0.07 (ii) 0.11	0.27 0.29	$\text{WO}_3$ precipitation in all cases. Made ammoniacal and reacidified before filtration.
5. Ammonium Carbonate No fusion Ignited residue extracted in 100 ml. ammonium carbonate, filtered and washed with 1% ammonium carbonate.	0.09	0.27	One member achieved good recovery by this method. Residues tend to be contaminated with $\text{WO}_3$ and $\text{MoO}_3$ .
6. Ammonium Hydroxide Ignited residue extracted in 100 ml. $\text{NH}_4\text{OH}$ (1:1), filtered and washed with 5% $\text{NH}_4\text{OH}$ .	0.14	0.29	$\text{WO}_3$ and $\text{MoO}_3$ incompletely extracted and tendency to become colloidal.
7. Alkali Carbonate Fusion Residue ignited, fused with 2 g. $\text{Na}_2\text{CO}_3$ , extracted in 100 ml. water, evaporated to fumes with 15 ml. $\text{HClO}_4$ . Extracted with 120 ml. 20% $\text{HCl}$ , filtered, washed and re-ignited.	0.14	0.30	No separation of $\text{SiO}_2$ and $\text{WO}_3$ and $\text{MoO}_3$ .
8. Extraction in Ammonium Citrate	—	—	Almost complete solution of $\text{SiO}_2$ .

The certificate figures given by the standardising body for the two B.C.S. steels in the foregoing experiments are: B.C.S. 167, 0.12-0.15% Si, and B.C.S. 220, 0.27-0.32% Si.

TABLE IV.—RESULTS OBTAINED BY THE SUB-COMMITTEES USING THE FINAL METHOD FOR SILICON

Steel Type	% Silicon—Analyst								
	A	B	C	D	E	F	G	H	I
3% Si Haematite Iron .. ..	3.81	3.81	3.83	3.83	3.79	3.81	3.81	3.79	3.81
1% Si Basic Iron .. ..	0.58	0.59	0.59	0.59	0.58	0.58	0.59	0.59	0.59
18/8 + 1½% Nb .. ..	0.67	0.68	0.67	0.67	0.68	0.68	0.67	0.68	0.68
14% Cr + 0.1% Zr .. ..	0.50	0.50	0.50	0.49	0.51	0.48	0.49	0.50	0.49
25% Cr, 20% Ni .. ..	1.65	1.66	1.66	1.64	1.66	1.67	1.66	1.66	1.66
18/8 + 1½% Ti + 1% Al .. ..	0.97	0.98	0.96	0.97	0.96	0.98	0.97	0.97	0.96

Attempts to prevent tungstic acid interference by forming soluble tungsten complexes with citric and tartaric acids in the initial steel solution, thus inhibiting hydrolysis, also failed, as complete dehydration of silicic acid was prevented. Complex formation with phosphoric acid was considered impracticable, owing to the marked attack of this reagent on glassware during fuming.

### Conclusions

It is considered that the results obtained in tests of the method described in Appendix III provide sufficient evidence of its precision and general applicability to the wide range of steel and iron compositions on which it has been tested, with the exception of high tungsten and tungsten-molybdenum steels, and the method has now been approved for submission to the British Standards Institution.

## MANGANESE

### Introduction

This investigation was also conducted in its early stages by the Panel of the Analysis Sub-Committee<sup>1</sup> and was later continued and completed by the Pig Iron and Low Alloyed Steels Analysis Sub-Committee and the Highly Alloyed Steels and Ferro-Alloys Analysis Sub-Committee.<sup>2</sup>

It was recognised that for maximum application to alloy-steel compositions, some form of separation method would be necessary, and attention was directed to an examination of variants of the zinc-oxide separation procedure, with persulphate oxidation to permanganic acid, followed by titration.

### Details of Investigation

**Zinc oxide separation.**—Separations were made from perchloric acid and from sulphuric-acid solution, with and without partial neutralisation with ammonium hydroxide and ammonium or sodium carbonate.

Perchloric acid is useful for decomposing carbides, and sharp separations of iron and chromium can be made under proper conditions, but two features arise in connection with its use.

- (a) A considerable amount of chloride is formed as a decomposition product of the fuming acid, and a rather critical oxidation of the fuming solution is necessitated, otherwise a large amount of silver chloride is precipitated, and the persulphate oxidation may be incomplete due to silver ion impoverishment
- (b) The perchloric acid-fumed solution contains chromium in the hexavalent condition, and all chromium must be reduced to the trivalent condition, otherwise positive errors arise due to escape of chromate into the zinc-oxide filtrate. Reduction of hexavalent chromium requires substantial amounts of sulphurous acid for high-chromium steels, and if simultaneous partial



reduction of ferric iron occurs, a faulty zinc-oxide separation results, due to incomplete hydrolysis of iron.

It was, therefore, decided to operate zinc-oxide separations in sulphuric-acid medium. It appeared to be immaterial whether the free acidity was neutralised in part with ammonia, ammonium carbonate or other alkali, before completing the hydrolysis with zinc-oxide emulsion, but providing the free acid was kept within suitable limits, it was considered safer to avoid the use of alkali and use zinc oxide alone for the complete neutralisation process.

Other features of the zinc-oxide separation which have received attention are:—

- (a) Low results were occasionally recorded with high-manganese steels—e.g., 18% chromium, 9% manganese, and the possibility of adsorption losses of manganese in the zinc-oxide group precipitate was considered. Examination of this feature showed no evidence pointing to the direct occlusion of manganese in the precipitate, but it was noted that strong fuming of the initial solution sometimes caused the formation of traces of manganese as insoluble hydrated dioxide. This was prevented by the simple expedient of adding a few drops of sulphurous acid to the extract of the fumed concentrate and provision for this is now incorporated in the method. There is no danger of further loss of manganese due to atmospheric oxidation at the zinc-oxide separation stage. This point was proved under severe conditions by conducting a stream of oxygen through the solution before completing the zinc-oxide separation.
- (b) The possibility of significant volume changes arising from variations of solution temperature has been examined, and whilst the evidence indicates that the zinc-oxide neutralisation reaction is exothermic, the temperature increment in relation to the total solution volume is not sufficient to affect the accuracy with which aliquots can be collected from the bulk solution. This is illustrated by the figures given in Table V.

TABLE V.—TEMPERATURE VARIATION DURING ZINC OXIDE SEPARATION

Temp. of Sol. before separation	Temp. of Sol. after separation	Temp. of Sol. after dilution to 500 ml. and standing 5 mins.	Temp. of a 250 ml. filtered fraction
21° C.	34° C.	27.5° C.	25.5° C.
17 "	32 "	26.5 "	25.0 "
18 "	32 "	27.0 "	26.0 "
20 "	33 "	26.5 "	26.0 "
20 "	34 "	26.5 "	26.0 "

- (c) It is recognised that a minor volume error arises due to the volume occupied by the solid matter—i.e., the precipitated hydroxides and excess zinc oxide suspended in the mother liquor when the solution is made up to bulk. It is calculated that 2.2g. of sample will account approximately for a volume of 5.5 ml., equivalent to an error of approximately 1% of the amount of manganese being determined. It has often been common practice to make some arbitrary correction of the solution volume, but it is considered that greater consistency is obtained by diluting exactly to the graduation mark. The practical effect of a consistently small error of 1% will not affect the permissible accuracy tolerances, as the effect is

reduced pro rata for high-manganese steels, which are operated on reduced initial sample weights. (See Note 1 to the Method).

- (d) Silver nitrate is added to the solution before filtration of the iron group precipitate, as in this way the solution is rendered free from residual chloride and the excess of silver ion subsequently provides the catalyst for the persulphate oxidation.
- (e) In applying the separation to solutions deficient in iron—e.g., nickel-base alloys of the nichrome type, tests were made to ascertain the efficiency of the zinc-oxide hydrolysis of chromium in the relative absence of iron. Table VI shows the results of a series of tests on an 80/20 nickel-chrome alloy, with and without an addition of 1g. equivalent of iron. The results show that no addition of iron is necessary in making separations of chromium from manganese.

TABLE VI.—RESULTS ON 80/20 NI-CR ALLOY—ZnO SEPARATION WITH AND WITHOUT ADDED IRON

Analyst	Without addition of iron	With 1 g. iron added
A .. .. .	0.10	0.10
B .. .. .	0.14	0.11
C .. .. .	0.10	0.10
D .. .. .	0.10	0.11
E .. .. .	0.11	0.15
F .. .. .	0.10	0.11
G .. .. .	0.10	0.10

*Persulphate oxidation of manganese.*—A careful study has been made of the critical features of the silver-ammonium persulphate oxidation of manganese solutions to permanganic acid, with particular reference to the duration of the boiling interval and the intensity of ebullition. It is difficult to define the conditions of the boiling period in terms sufficiently precise to ensure a practical application, within limits which prevent partial decomposition of permanganic acid with attendant low results, on the one hand, and retention of residual undecomposed persulphate and resultant high values, on the other.

A high acidity in the solution, particularly of phosphoric acid, has been a decided advantage in promoting maximum stability of permanganic acid, and the need for maintaining a high silver ion concentration in test fractions, as a contributory factor in preventing partial decomposition of permanganic acid in manganese rich solutions, is also important.

The effect of boiling time on the persulphate oxidation is shown graphically in Fig. 1, and a selection of typical test results are shown in Table VII. It is clear that traces of residual persulphate remain for at least 10 minutes after the reagent addition and that 15 minutes is the optimum safe boiling period for its complete decomposition. The presence of residual persulphate in

TABLE VII.—EFFECT OF BOILING PERIOD ON THE PERSULPHATE OXIDATION OF MANGANESE

Steel Type	Boiling Period—Minutes										Remarks
	2	5	7	9	10	11	13	15	20		
34% Si Haematite iron	1.63	1.56	1.50	1.46	—	1.44	1.43	1.42	1.42	Av. of	
1% Si Basic iron	1.23	1.16	1.11	1.09	—	1.08	1.07	1.07	1.06		
18/8 + 14% Mn (direct titration)	—	—	—	—	1.54	—	—	1.525	—	several	
18/8 + 14% Mn (back titration)	—	—	—	—	1.36	—	—	1.325	—	deter-	
Low manganese (direct titration)	—	—	—	—	0.055	—	—	0.054	—	mina-	
Low manganese (back titration)	—	—	—	—	0.07	—	—	0.055	—	tions	

10-minute tests can be further demonstrated by re-titrating the titrated solutions after standing, when a further consumption of ferrous sulphate may be recorded due to continued slow oxidation by the undecomposed persulphate. With boiling periods exceeding 20 minutes, there is gradual but progressive decomposition of permanganate.

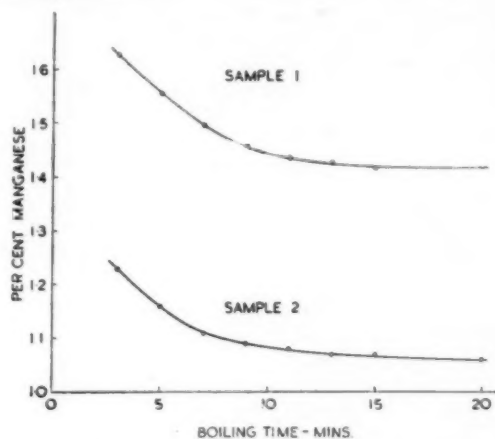


Fig. 1.—Effect of boiling time on persulphate oxidation of manganese.

**Effect of cobalt.**—An interesting observation noted during the early work was that in the presence of appreciable cobalt there occurred a partial simultaneous oxidation of this element from the bivalent to the tervalent state under the conditions initially specified, the effect of which was to induce a positive error, equivalent to 0.01–0.02% manganese. The three cobalt steels of the test series all showed manganese values rather higher than the corresponding values by the absorptiometric procedure, whereas cobalt-free steels of the series gave, within normal tolerances, identical values by the two methods. This is illustrated by the figures in Table VIII.

TABLE VIII.—EFFECT OF COBALT ON MANGANESE DETERMINATION

Steel	Mean % Manganese	
	Volumetric	Absorptiometric
Plain carbon .. .. .	0.725	0.72
4% Silicon .. .. .	0.20	0.20
14% Chromium .. .. .	0.195	0.20
18/8 + 3% Mo .. .. .	0.415	0.42
18/8 + 14% Nb .. .. .	0.425	0.42
14% Cr + 0.1% Zr .. .. .	0.47	0.465
14% Cr, 14% Cr, 34% Co ..	0.39	0.375
16% W, 4% Cr, 4% Co ..	0.25	0.235
7% W, 4% Mo, 0.6% Co ..	0.265	0.25

Further confirmation of the validity of this observation was obtained from experiments with synthetic manganese-cobalt mixtures (Tables IXA and B) and in particular these experiments indicated that the effect was independent of the presence of zinc ion and also that the degree of tervalent cobalt formation was a function of the acidity of the solution, and that by sufficiently increasing the latter, cobalt oxidation could be inhibited without prejudice to the oxidation of manganese. The value of high acidity in preventing cobalt interference is, therefore, complementary with its alternative function of promoting maximum stability of the permanganic acid.

TABLE IX A.—SUPPRESSION OF INTERFERENCE OF COBALT IN SYNTHETIC SOLUTIONS BY INCREASE IN ACIDITY

Acid Mixture Added	% Cobalt Added	% Manganese	
		Added	Found
15 mls.	nil	0.50	0.50
15 mls.	10%	0.50	0.52
15 mls.	10%	nil	0.02
20 mls.	10%	0.50	0.51
30 mls.	10%	0.50	0.50
40 mls.	10%	0.50	0.49

TABLE IX B.—SUPPRESSION OF INTERFERENCE OF COBALT ADDED TO STEELS BY INCREASE IN ACIDITY

Steel	% Mn	Acid Mixture Added	% Manganese Found	
			No Co	10% Co added
BCS 211 (14% Cr)	0.54	15 ml.	0.35	0.37
	0.54	30 ml.	0.34	0.35
	0.54	40 ml.	0.35	0.34
P.S.T. (18/8 + 1/2% W)	0.54	15 ml.	0.55	0.57
	0.54	30 ml.	0.54	0.54
	0.54	40 ml.	0.53	0.54

A secondary effect of cobalt arises from the interference of the pink cobalt ion with accurate detection of titration end points using potassium permanganate.

Various devices have been examined for improving end-point detection in cobalt-rich solutions. Indicators such as disulphine blue and orthophenanthroline-ferrous complex showed improvement, and some success was achieved by introducing nickel sulphate in amount equivalent to three times the amount of cobalt present, which masked the pink of the cobalt ion by the green of the nickel ion. This was not an ideal solution of the problem as the intensely green nickel solutions caused some reduction of end-point sensitivity, and ultimately permanganate titration was abandoned in favour of potassium dichromate with barium diphenylamine sulphonate indicator. This proved successful, and good end-point detection was obtained with titration solutions from 35% cobalt steels, 80/20 nickel-chrome alloy, etc., and since potassium dichromate is a primary salt of high purity, and of greater stability than permanganate, its use was generally adopted for all final confirmatory tests on steels.

**Effect of other elements.**—There is no significant interference from other elements. The influence of vanadium in amounts up to 2% is shown to be negative (Table X). Tungstic acid or other insoluble matter, if present in substantial quantity, should be removed, otherwise the progress of the zinc-oxide neutralisation may be obscured.

TABLE X.—EFFECT OF VANADIUM

Analyte	35% Co Magnet Steel	
	Without vanadium addition	With equiv. of 2% V. added
A .. .. .	0.71	0.721
B .. .. .	0.70	0.69
C .. .. .	0.695	0.695
D .. .. .	0.69	0.69

## Results

Results on a wide range of steels are given in Table XI. These results were obtained by the Analysis Sub-Committee Panel<sup>1</sup> before the method was evolved in its final form. The final test results, using the method exactly as described in Appendix IV are shown in Table XII.

TABLE XI.—TYPICAL RESULTS OBTAINED BY THE SILICON-MANGANESE PANEL USING THEIR DRAFT METHOD FOR MANGANESE

Steel Type	Analyst					
	A	B	C	D	E	F
Plain carbon .. .. .	0.74	0.73	—	0.72	0.71	0.74
4% Si .. .. .	0.20	0.20	—	0.20	0.19	0.20
14% Cr .. .. .	0.20	0.20	—	0.20	0.18	0.20
Low Si, High S .. .. .	1.13	1.14	—	—	—	1.13
25% Cr, 20% Ni .. .. .	0.92	—	—	0.93	—	—
18/8 + 14% Ti + 1% Al .. .. .	0.64	0.64	—	0.63	—	0.64
C, Cr, Co .. .. .	0.42	0.41	0.41	0.41	0.38	0.41
16% W high speed .. .. .	0.26	0.25	0.25	0.25	0.23	0.26
7% W, 4% Mo, high speed .. .. .	0.27	0.25	0.26	0.27	0.25	0.28
18/8 + 3% Mo .. .. .	0.43	0.41	0.40	0.41	0.40	0.44
18/8 + 14% Nb .. .. .	0.43	0.44	0.43	0.43	0.40	0.43
14% Cr + 0.1% Zr + 8 .. .. .	0.47	0.47	0.47	0.47	0.47	0.48
13% Mn .. .. .	13.5	—	13.3	—	13.4	13.6
17% Co .. .. .	0.18	0.17	0.16	—	—	0.18

TABLE XII.—RESULTS OBTAINED BY THE SUB-COMMITTEES USING THE FINAL METHOD FOR MANGANESE

Steel Type	Analyst									
	A	B	C	D	E	F	G	H	I	J
34% Si haematite iron .. .. .	1.43	1.46	1.44	1.40	1.40	1.43	1.45	1.42	1.41	1.43
14% Si Basic iron .. .. .	1.10	1.09	1.08	1.08	1.07	1.06	1.12	1.12	1.07	1.08
14% C, 14% Cr, 24% Co .. .. .	0.41	0.40	0.38	0.41	0.38	0.41	0.41	0.41	0.40	0.39
18/4/1 high speed .. .. .	0.29	0.29	0.26	0.28	0.26	0.30	0.30	0.28	0.27	0.29
18/8 + 14% Mn .. .. .	1.52	1.51	1.56	1.54	1.50	1.54	1.55	1.55	1.56	—
14% Cr, 0.1% Zr .. .. .	0.45	0.46	0.48	0.46	0.46	0.47	0.48	0.47	0.47	—
25% Cr, 20% Ni .. .. .	0.92	0.95	0.95	0.92	0.93	0.93	0.95	0.94	0.95	—
18/8 + 14% Ti + 1% Al .. .. .	0.64	0.63	0.66	0.64	0.65	0.63	0.65	0.65	0.65	—
18% Cr, 9% Mn .. .. .	9.24	9.22	9.19	9.21	9.22	9.16	9.21	9.21	9.16	—
25% Co magnet alloy .. .. .	0.71	0.70	0.70	0.69	0.70	0.69	0.68	0.69	0.70	—
25% Co magnet alloy .. .. .	0.14	0.13	0.13	0.13	0.14	0.13	0.14	0.13	0.12	—
80/20 Ni-Cr alloy .. .. .	0.11	0.11	0.115	0.115	0.115	0.12	0.115	0.11	0.10	—

### Conclusion

The method of Appendix IV has been tested and confirmed on a wide variety of steels and has been accepted by the Methods of Analysis Committee and submitted to the British Standards Institution for approval as a standard method.

### APPENDIX I

Constitution of the Silicon-Manganese Panel, Standard Methods of Analysis Sub-Committee, Heterogeneity of Steel Ingots Committee, Iron and Steel Institute, at July 15th, 1946.

Mr. B. Bagshawe (Convenor), Brown-Firth Research Laboratories.

Mr. S. Harrison, Kayser Ellison & Co., Ltd.

Mr. J. D. Hill, Bragg Laboratory.

Mr. A. P. Lunt, Park Gate Iron & Steel Co., Ltd.

Mr. C. W. Short, John Lysaght, Ltd.

Mr. J. L. West, Hadfields, Ltd.

### APPENDIX II

Constitution of the Co-operating Sub-Committees of the Methods of Analysis Committee, Metallurgy Division, B.I.S.R.A., at September 30th, 1947.

*Pig Iron, Carbon and Low-Alloyed Steels Analysis Sub-Committee*

Mr. J. H. Wright (Chairman), Dorman Long & Co., Ltd.

Mr. O. Beadle, Cargo Fleet Iron Co., Ltd.

Mr. W. F. Charteris, Colvilles, Ltd.

Mr. S. W. Craven, I.C.I. Ltd., Alkali Division.

Mr. J. M. Harrison, Lancashire Steel Corporation, Ltd.

Mr. J. D. Hill, Bragg Laboratory.

Mr. B. W. Methley, Steel Peech & Tozer, Ltd.

Mr. H. R. Pepper (Vice-Chairman), Stewarts & Lloyds, Ltd.

Mr. N. D. Ridsdale, Bureau of Analysed Samples, Ltd.

Mr. H. Thomas, Richard Thomas & Baldwins, Ltd.

Mr. W. Westwood, British Cast Iron Research Assoc.

### Highly Alloyed Steels and Ferro-Alloys Analysis Sub-Committee

Mr. B. Bagshawe (Chairman), Brown-Firth Research Laboratories.

Dr. J. Cameron, Clyde Alloy Steel Co., Ltd.

Mr. W. T. Elwell, I.C.I., Ltd. Billingham Division.

Mr. L. E. Gardner, Edgar Allen & Co., Ltd.

Mr. S. Harrison, Kayser Ellison & Co., Ltd.

Mr. J. D. Hill, Bragg Laboratory.

Mr. G. Murfitt, Wm. Jessop & Sons, Ltd.

Mr. R. Postlethwaite, Samuel Fox & Co., Ltd.

Mr. T. E. Rooney, National Physical Laboratory.

Mr. J. L. West, Hadfields, Ltd.

### APPENDIX III

The Determination of Silicon in Pig Iron and all types of Plain and Alloy Steel other than high tungsten and high tungsten-molybdenum steels—(now published as B.S.1121, Part 10).

#### Section 1—Introduction

(a) *Principle.* A hydrochloric-acid solution of the sample is fumed with perchloric acid. The silica, thus dehydrated and rendered insoluble, is removed by filtration and weighed after ignition in a platinum crucible. Accurate estimation of the silica is obtained by the loss in weight after its removal as silico-fluoride.

(b) *Range.* Up to 4.0% with 5 g. sample.

(c) *Reproducibility.*

With 0.01% silicon present  $\pm 0.002\%$  silicon.

With 0.20% silicon present  $\pm 0.01\%$  silicon.

With 4.0% silicon present  $\pm 0.02\%$  silicon.

The method is not accurate in the presence of high tungsten or molybdenum contents owing to the volatility of their oxides at comparatively low temperatures.

#### Section 2—Reagents Required

All reagents shall be of guaranteed purity and distilled water shall be used throughout. Solutions shall be freshly prepared.

##### Solutions

*Hydrochloric acid* (1 : 4). Dilute 200 ml. of hydrochloric acid (sp. gr. 1.16) to 1 litre.

*Sulphuric acid* (1 : 3). Add 25 ml. of sulphuric acid (sp. gr. 1.84) to 50–60 ml. of water, cool and adjust the volume to 100 ml. with water.

#### Section 3—Sampling

Recommended methods of obtaining a suitable sample for the analytical procedure outlined in Section 4 are described in B.S. .... \*

#### Section 4—Procedure

Transfer 5 g. of sample (Note 1) to a covered 400-ml. squat, resistance-glass beaker. Add 50 ml. of hydrochloric acid (sp. gr. 1.16), digest until dissolved and then oxidise by dropwise additions of nitric acid (sp. gr. 1.42).

Add 50 ml. of perchloric acid (sp. gr. 1.54) and, with the beaker covered, evaporate to fumes of the acid and continue fuming for 10–15 minutes at such a temperature as will maintain a steady reflux of acid on the walls of the beaker.

Allow to cool and extract the fumed mass by warming with 20 ml. of hydrochloric acid (sp. gr. 1.16), or such an amount as may be found necessary to reduce all chromium to the trivalent condition. Dilute with 150 ml. of cold

\*In course of preparation.



water and if necessary warm gently to ensure complete solution of soluble salts.

Filter through a paper-pulp pad, rinse the beaker with washes of hot hydrochloric acid (1:4), removing adherent particles of silica by vigorous action with a 'policeman,' and finally wash the filter several times with hot hydrochloric acid (1:4) and cold water used alternately. Continue the washing until the filter is free from iron salts, collect the filtrate together with all washings in a 600-ml. squat, resistance-glass beaker. Reserve the pad—Residue A.

Evaporate the filtrate to fumes (Note 2), maintain the fuming period as previously described, extract, filter through a separate pad, wash, etc., as in the first dehydration—Residue B.

Transfer the two filters to a platinum crucible and ignite at a low temperature until carbonaceous matter is removed and finally in a muffle furnace at a temperature of not less than 1,000° C. Cool in a desiccator and weigh. Repeat the ignition until constant weight is obtained.

Just moisten the residue with water, add four drops of sulphuric acid (1:3) (Note 3) and, depending upon the silicon content, add 2–4 ml. of hydrofluoric acid. Evaporate to dryness and ignite to constant weight at the same temperature and under the same conditions as in the first ignition.

A simultaneous blank determination on all reagents should be carried through all stages of the process, and its weight deducted from the test weight before making the calculation. (Note 4).

#### Section 5—Calculation

Let X = weight of crucible and residue after ignition.

Y = weight of crucible and residue after hydrofluoric acid treatment.

P = weight of crucible and residue from blank determination.

Q = weight of crucible and residue from blank determination after hydrofluoric acid treatment.

Then—weight of silica from 5 g. sample =  $X - Y = M$

weight of silica from reagents =  $P - Q = N$

Percentage of silicon in steel =

$$\frac{(M - N) \times 0.4672 \times 100}{5} \\ = 9.344 (M - N)$$

#### Section 6—Notes

1. In the case of pig iron, sieve the drillings, using a 60-mesh sieve, weigh each portion and calculate the ratio of coarse to fine. Weigh out amounts of the coarse and fine portion in this ratio to make up the 5 g. sample.

2. The efficiency of perchloric acid dehydration under the conditions specified has been shown to be such that an average amount of considerably less than 1 mg. of silica remains unrecovered after a single dehydration. It is recommended that for standard purposes, and in all cases where maximum precision is necessary, a second evaporation, and recovery of traces of residual silica, be made according to the provisions laid down in the Procedure. The need for a second evaporation is recognised to be of minor importance for purposes of general routine control and its retention or deletion for this purpose may be left to the discretion of the analyst.

3. For columbium (niobium) bearing steel, up to 2 ml. of sulphuric acid (1:3) should be used to prevent loss of columbium (niobium). The subsequent ignition also

requires great care to prevent mechanical loss by decrepitation, and it is advantageous to make use of a radiant heater.

4. If an appreciable "blank" is obtained, individual reagents should be tested and a fresh supply substituted for unsatisfactory material.

### APPENDIX IV

Tentative Standard Method for the Determination of Manganese in Iron and Steel.

#### (1) Introduction

(a) *Principle.*—The sample is dissolved in dilute sulphuric acid, any other acid additions necessary for complete solution being removed by fuming after oxidation, and a zinc-oxide separation is made. The resultant solution is strongly acidified to prevent interference from cobalt and oxidised with ammonium persulphate. The permanganic acid is titrated using ferrous-ammonium sulphate and potassium dichromate, with barium diphenylamine sulphonate as indicator.

(b) *Range.*—Up to 14% with appropriate sample weights.

(c) *Reproducibility.*

With 0.1% manganese present,  $\pm 0.005\%$  manganese

" 1.0% " "  $\pm 0.01\%$  "

" 10.0% " "  $\pm 0.07\%$  "

" 14.0% " "  $\pm 0.10\%$  "

(d) The method has been applied to a very wide range of plain and alloy irons and steels with satisfactory results.

#### (2) Special Apparatus Required

Grade A graduated glassware should be used throughout.

#### (3) Reagents Required

(a) All reagents shall be of guaranteed purity and distilled water shall be used throughout. Solutions should be freshly prepared and, where necessary, filtered.

(b) *Solutions.*

*Sulphuric acid* (3:17).—To about 800 ml. of water, add 150 ml. of sulphuric acid (sp. gr. 1.84), cool and dilute to 1 litre.

*Sulphurous acid.*—Pass sulphur dioxide gas into water until a saturated solution is obtained.

*Silver nitrate* (1%).—Dissolve 10 g. of silver nitrate in water and dilute to 1 litre.

*Phosphoric-sulphuric acid.*—To 330 ml. of water, cautiously add 330 ml. of phosphoric acid (sp. gr. 1.75) and 330 ml. of sulphuric acid (sp. gr. 1.84), cool and dilute to 1 litre.

*Ammonium persulphate* (12.5%).—Dissolve 125 g. of ammonium persulphate in water, and dilute to 1 litre.

*Indicator.*—Dissolve 0.37 g. of barium diphenylamine sulphonate in 90 ml. of hot water, cool and dilute to 100 ml.

*Ferrous ammonium sulphate* (N/10 approx.).—Dissolve 40 g. of ferrous ammonium sulphate ( $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ) in a mixture of 500 ml. of water and 20 ml. of sulphuric acid (sp. gr. 1.84), cool and dilute to 1 litre.

*Potassium dichromate* (N/10).—Dissolve 4.903 g. of potassium dichromate (crushed and dried for 1 hour at 130° C.) in 500 ml. of water and dilute to exactly 1 litre.

(1 ml. of this solution = 0.0011 g. of manganese).

**Zinc oxide emulsion.**—Shake 50 g. of zinc-oxide powder with sufficient water to make a thin cream.

#### (4) Sampling

Recommended methods of obtaining a suitable sample for the analytical procedure outlined below are described in B.S. 684.\*

### (5) Procedure

Transfer 2.2 g. of sample (Note 1) to a 750-ml. Taylor pattern flask and digest with 70 ml. of dilute sulphuric acid (3 : 17) (Note 2) until dissolution of the metal is complete and only a residue of carbides remains undecomposed.

Oxidise with nitric acid (sp. gr. 1.42) added dropwise, evaporate to fumes of sulphuric anhydride and cool. Extract the fumed concentrate with 150 ml. of water, add 5 drops of sulphurous acid solution, boil for a few minutes to ensure complete solution of sulphates and cool to room temperature (Note 3).

Without further dilution add zinc-oxide emulsion with intermittent shaking until the solution is neutralised and the iron group hydroxides are precipitated. Allow a moderate excess of zinc oxide, add 35 ml. of silver-nitrate solution (1%), shake, transfer to a 500 ml. graduated flask, make up to the mark with water, mix and allow to stand for 5 minutes.

Collect a 250 ml. fraction by filtration through a dry, fluted 24-cm. Whatman No. 12 paper, discarding the first runnings. Transfer the fraction to a 500-ml. Taylor-pattern flask and add 30 ml. of phosphoric-sulphuric acid mixture. Heat to boiling, add cautiously 20 ml. of ammonium persulphate solution (12.5%), boil the solution for a timed period of 15 minutes (Note 4), and cool rapidly to room temperature.

Titrate the cold solution with ferrous ammonium-sulphate solution (N/10 approx.) using a minimum of 2 ml. excess, add 5 drops of indicator solution and back-titrate with potassium dichromate solution (N/10) to a deep violet colour.

### (6) Standardisation

Transfer 30 ml. of phosphoric-sulphuric acid to a 500-ml. Taylor-pattern flask, dilute to 300 ml. and add 5 drops of indicator solution. Add one drop ferrous ammonium-sulphate solution (N/10 approx.) and 2 drops potassium-dichromate solution (N/10). A deep violet colour should be obtained (Note 5). Add more ferrous-ammonium sulphate (N/10 approx.) to a total of 25 ml. and back titrate with potassium-dichromate solution (N/10) to a deep violet end-point, recording the total volume of potassium-dichromate solution added.

### (7) Calculation

(a) *Standardisation.*

Volume of ferrous ammonium-sulphate solution added = 25 ml.

Let volume of potassium-dichromate solution (N/10) added = X ml.

Then normality of ferrous ammonium-sulphate solution =  $X/25.N/10$ .

(b) *Determination.*

Let volume of ferrous ammonium-sulphate solution added = A ml.

Let volume of potassium-dichromate solution (N/10) added = 3 ml.

Then volume of standard solution (N/10) equivalent to manganese in 1.1 g. of sample =  $AX/25 - B$ .  
i.e., Manganese per 100 g. sample =  $(AX/25 - B) \times 0.0011 \times 100/1.1$  g., or manganese in sample =  $(AX - 25B)/250\%$

(c) The manganese content should be reported as a percentage to two places of decimals.

### (8) Notes

1. Sample weights should be adjusted as follows :—

Up to 4%	manganese content	—2.2 g. of sample
4-8%	" "	1.1 g. of sample
Over 8%	" "	0.55 g. of sample

2. (a) Sulphuric acid (3 : 17) gives satisfactory solvent action on all plain, low alloy and the simpler types of rustless steels. Solution becomes progressively more difficult with increasing nickel content. It is permissible to make additions of both hydrochloric and nitric acids to speed up solution in difficult cases, but in such instances it is important that complete expulsion of hydrochloric acid be achieved at the fuming stage. This is more certain if the fumed concentrate is taken up with about 30 ml. of water and the evaporation to fumes repeated.

(b) Stainless-type steels which are not treated with hydrochloric acid must not be oxidised until solution of the metal is complete, otherwise a state of passivity will be induced, and further solution will be arrested. Solutions of steel of this type must be fumed before oxidation.

(c) In the majority of cases, the carbide residue responds to oxidation with nitric acid followed by fuming. Certain classes of high carbon chromium alloys of the tool and die-steel class leave large residues of very resistant carbide which are not always completely decomposed by this treatment.

In such cases, it is recommended that the solution be given an extended period of hot digestion prior to oxidation with nitric acid, or alternatively the solution in sulphuric acid may be evaporated to fumes in the ferrous condition, and subsequently oxidised with nitric acid after extracting the sulphates, and the evaporation to fumes repeated.

(d) The evaporation to fumes may be omitted for plain-carbon and nickel steels, but for standard purposes it is recommended that it should be carried out.

3. If a substantial precipitate of tungstic acid is noticeable at this stage, it is recommended that it should be removed before proceeding. Filter through a pulp pad and wash with small amounts of cold-dilute sulphuric acid (1 : 39). Discard the residue and proceed with the filtrate as in paragraph 3 of the method procedure.

4. The addition of glass beads or small pieces of silica brick is recommended as an aid to controlled ebullition.

5. If this colouration is not obtained, the presence of reducing matter in the water, phosphoric acid or sulphuric acid should be suspected, and fresh supplies procured.

<sup>a</sup>In course of preparation.

# MICROANALYSIS

CHEMICAL AND PHYSICAL METHODS

APPARATUS

METALLURGICAL APPLICATIONS

TECHNIQUE

"WE believe the time has arrived when it is necessary to provide periodic reviews of the scientific literature on analytical chemistry as an essential supplement to the publication of original research." With these words, our contemporary, "Analytical Chemistry," introduces yet another progressive step in its policy. In past years, "Analytical Chemistry" has published, from time to time, but without any defined policy, reviews which we have regarded as one of the most valuable of its services to the analytical chemist. Anyone familiar with these, or with the review articles which have formed a considerable part of the matter of these columns, will be well aware that the literature of analytical chemistry is so extensive that to keep in touch with the whole field is practically a full time job. In future, research workers must more and more rely on the services of reviewers, more particularly if these are critical in their work. So often at present a problem is shelved simply because the researcher fears that it might already have been tackled elsewhere; but the literature hunt necessary to determine this is too time-consuming. We are gratified to find that the attitude to review articles which we expressed explicitly some time ago, and which is implicit in our policy, is endorsed in this way by our distinguished contemporary. We look forward with interest and keen anticipation to reading the first of these articles in the issue for January, 1949.

## Micro Methods for the Determination of Halogens

By J. H. Beaucourt

*A review is given of the numerous methods which have been applied to the determination of organic halogen. These offer a range of finishes which includes gravimetric, volumetric and potentiometric titration procedures.*

IN organic microanalysis there are probably more methods available for the determination of the halogens than for any other element. Some are of universal application, but others may only be used in certain cases, being limited by the characteristics of the type of compound being analysed. Factors of importance in the latter case are usually volatility and the nature of the elements, other than halogens, present in the compound.

The methods which have been advanced are as follows:

- (1) Combustion methods.
- (2) Carius methods.
- (3) Bomb methods.
- (4) Sulphuric acid decomposition methods.
- (5) Stepanow methods.
- (6) Hydrogenation methods.
- (7) Miscellaneous methods.

Methods depending on combustion in a bomb, including lime-fusion methods, have already been dealt with in a

previous article by the present author<sup>1</sup> and will not be considered further.

### Combustion Methods

Methods based on this principle are probably the most important since they can be applied to all types of compound. The first of such micro-methods was developed by Pregl, being based on the macro-methods developed earlier by Dennstedt. In the Pregl method the compound is combusted in a tube and the decomposition products passed over heated platinum catalysts. The halogens are absorbed in sodium carbonate and sodium bisulphite solution and finally determined gravimetrically as the silver halide. Because of the difficulty experienced with the iodine determination Leipert<sup>2</sup> developed an alternative finish to the method. The combustion is effected in the same manner, but the iodine is absorbed

<sup>1</sup> Beaucourt, *Metallurgia*, 1945, **32**, 181-184.  
<sup>2</sup> Leipert, *Biochem. Zeits*, 1935, **281**, 436.



in a solution of sodium hydroxide. The iodide is then oxidised to iodate with bromine, the excess bromine destroyed by formic acid, excess potassium iodide added and the liberated iodine titrated with standard thio-sulphate.

The reactions may be summarised as follows :—



Thus six times the original amount of iodine is liberated and a very favourable conversion factor obtained. Such a process is known as an *amplified* titration.

Bobranski<sup>3</sup> uses the same combustion process on the semimicro scale, but absorbs the halogens in heated barium carbonate in the case of chlorine and bromine, and in sodium sulphite solution in the case of iodine. The determinations are completed argentometrically, using dichlorofluorescein as indicator for the chlorine and eosin for bromine and iodine.

Hölscher<sup>4</sup> uses a similar method, but absorbs in hydrogen peroxide. Adsorption indicators are also used, but whereas Bobranski uses a weight burette for the titration, Hölscher prefers the conventional micro-burette and more dilute solution.

Modifications to the combustion process have been devised such as combustion in a quartz tube at the surface of silica frits<sup>5</sup> or even combustion in an empty tube using a fast flow of oxygen.<sup>6</sup> These methods have the advantage of speed, but it is not yet known if they can be applied to all types of organic compound.

Some investigators prefer to absorb the halogen on metallic silver in which case the increase of weight of the silver is determined or the silver halide is extracted and then determined titrimetrically by some suitable method.<sup>7</sup>

#### Carius Method

A micro-method based on the classical Carius method was developed by Pregl in 1910. In this method the sample is decomposed in a sealed tube with nitric acid in the presence of silver nitrate. The silver halide produced is then isolated and weighed. Special precautions must be taken to avoid contaminating the precipitate with splinters of glass when the tube is being opened.

This method is undoubtedly the least popular of all the methods for the determination of the halogens because of the possibility of explosions and because more convenient methods are available. Although the defects of the procedure have been minimised and the time of heating reduced by later investigators<sup>8</sup> it is probable that the method will eventually become obsolete.

#### Sulphuric Acid Digestion Methods

In these methods the compound is decomposed with sulphuric and chromic acids in the presence of a silver catalyst, the liberated halogen being carried by a stream of air or oxygen into a suitable absorbent. Two micro methods using this principle have been developed : the Zacherl-Krainick<sup>9</sup> method and the Vieböck<sup>10</sup> method. Neither method can be used for iodine determination for under the conditions of the test this is converted to silver iodate and remains behind in the digestion flask. Both methods are also limited to the analysis of non-

volatile compounds, but have the advantage that little attention is required during the decomposition and an analysis may be completed in a little over half an hour.

In the Zacherl-Krainick method the decomposition is effected in a slow stream of oxygen, a mixture of potassium and silver chromates being added to the sulphuric acid which is maintained at 120° C. by heating in an aluminium block. The halogen is swept into the absorption apparatus, which contains a glass spiral to increase the path of the bubbles through the absorbent. The latter consists of hydrogen peroxide containing excess standard alkali. The reaction proceeds as follows :—



The unconsumed alkali is then titrated with standard acid.

In the method of Vieböck the apparatus is somewhat different in design and an air-stream is used to sweep out the halogens. Absorption is effected in hydrogen peroxide contained in three bubblers in series without alkali being present.

In Vieböck's method the acid produced is titrated directly with standard alkali, then a control titration is carried out by adding a saturated solution of mercuric oxycyanide to the neutral solution. The reaction proceeds as follows :—



The alkali liberated is proportional to the chloride or bromide present and may be titrated with standard sulphuric acid. The advantage of the control titration is that it is specific for chloride or bromide, whereas the first titration will include acid present from other sources, for example, in some cases undecomposed acetic acid may pass over from compounds containing acetyl groupings and it would be expected that nitro compounds might yield some nitrogen oxides which would be converted to nitric acid in the absorbent. No mention of this source of error is made by Zacherl and Krainick, but the present writer has obtained high results when nitro compounds are analysed, hence, it would seem that the Vieböck method is preferable when compounds containing other acid-forming elements besides halogens are being analysed. A useful apparatus has been designed by White which can be used for the Zacherl-Krainick method and also for the determination of alkoxy groups.

#### Stepanow Methods

The method of Stepanow in which the halogen is converted to the ionic form by decomposition of the sample with sodium and ethanol has been adapted successfully to the micro scale by Rauscher.<sup>11</sup> One difficulty associated with the original Stepanow method was the uncertainty of complete decomposition of the compound, the reaction between the ethanol and the compound with the sodium being competitive. The film of hydrogen bubbles which forms on the surface of the sodium can also inhibit its attack on the compound. To overcome this, various other solvents have been recommended but they have met with varying success. Rauscher found that a mixture of mono-ethanolamine and dioxane was extremely effective. The advantages of the method are its simplicity, only simple reflux apparatus being required, its comparative rapidity and its suitability for batch analysis. The determination is completed gravimetrically but, no doubt a titrimetric

<sup>3</sup> Bobranski, *Z. anal. Chem.*, 1931, **81**, 225; 1934 **35**, 99, 108.

<sup>4</sup> Hölscher, *Ind.*, 1934, **98**, 308.

<sup>5</sup> Schöberl, *Ang. Chem.*, 1937, **50**, 334.

<sup>6</sup> Belcher and Spooner, *J.C.S.*, 1943, 313.

<sup>7</sup> L'voort and Chang, *Bull. Soc. Chim. Belg.*, 1941, **50**, 115.

<sup>8</sup> Niederl, Baum, McCoy and Kuck, *Ind. Eng. Chem. (An. Ed.)*, 1940, **12**, 428.

<sup>9</sup> Zacherl and Krainick, *Mikrochemie*, 1932, **11**, 61.

<sup>10</sup> Vieböck, *Ber.*, 1932, **B85**, 496.

<sup>11</sup> Rauscher, *Ind. Eng. Chem. (An. Ed.)*, 1937, **9**, 296;

finish could be applied especially since Umhoefer<sup>12</sup> has advanced such a procedure on the macro scale. However, his procedure consists of neutralising the sodium hydroxide produced after the addition of water by nitric acid followed by titration with silver nitrate using dichlorofluorescein as indicator. As no attempt is made to counteract the effect of the large quantity of electrolyte present the end points would probably be very poor.

### Hydrogenation Methods

Lacourt<sup>13</sup> has described a hydrogenation method based on Ter Meulen's well-known macro method. The compound is reduced by hydrogen in the presence of nickel chromite catalyst. The hydrochloric acid produced is titrated with a standard solution of sodium borate using methyl red as indicator.

### Miscellaneous Methods

In the method of Willard and Thompson the compound is first sulphonated with fuming sulphuric acid to render it non-volatile and then decomposed with sulphuric acid and potassium persulphate. The chlorine is liberated by treatment with potassium permanganate, distilled into alkaline arsenite solution and finally precipitated and weighed as the silver salt.<sup>14, 15</sup> Bürger has used direct fusion with metallic potassium in a sealed tube,<sup>16</sup> a method which he has also applied to the determination of sulphur. Metallic sodium has also been used similarly on the macro-scale, and decomposition by metallic sodium in liquid ammonia.<sup>17</sup>

### Methods for Completing the Determination

The gravimetric method of weighing the silver halide is probably the least likely to give trouble, except in the case of iodine where the conversion factor is unfavourable. Titrimetric methods are generally preferred, however, being much more rapid. All the conventional argentometric methods have been applied—i.e., the Mohr method, the Volhard method and the adsorption indicator method, but each has certain disadvantages. Probably the Bobranski method using a weight burette is the best of this class, although the present writer prefers to use dichlorofluorescein as indicator for the titration of bromides instead of eosin for, in spite of the claims made for the latter indicator, the change is not well-marked especially with micro amounts.

Potentiometric titration methods appear to be the most convenient and accurate and have been widely used in Germany.<sup>18</sup>

The Leipter method discussed earlier in which an amplified titration is obtained is undoubtedly the best method for the determination of iodine. Bromine may be oxidised to bromate by hypochlorite and a similar amplified titration obtained, but the method has not been as widely used as it deserves. Both these methods are particularly useful because the atomic weights of these elements are high compared with that of chlorine and thus normally provide unfavourable titres.

The method of Lacourt *et al.* (loc. cit.) for completing the determination is an interesting modification of the Leipter method. After extraction of the silver halide with ammonia solution, a measured excess of standard potassium iodide is added to precipitate silver iodide.

The latter is filtered and the unconsumed iodide in the filtrate is oxidised to iodate and completed by the Leipter procedure.

Attempts have been made to apply a direct amplification titration to the determination of chloride using some such procedure as that of Sendroy<sup>18</sup> in which solid silver iodate is added to the chloride solution, to give the following reaction:—



After filtering and washing the insoluble silver chloride and iodate, the filtrate is treated with potassium iodide to give a six-fold yield of iodine. However, the comparative solubility of silver iodate causes serious errors in the method.

The limitations of alkalimetric titrations have already been discussed earlier.

### Determination of Mixed Halides

The need for determination of different halides occurring together is rarely encountered, although methods are available for such determinations. Moser and Miksch<sup>19</sup> collect the mixed precipitates of two halides in a Nebauer crucible and weigh. An excess of pure dry ammonium bromide or iodide is then added and heated to 300° C. Silver bromide or iodide is formed and the excess ammonium salt is eliminated simultaneously by volatilisation. From the two weighings the respective amounts of halide can be calculated.

Strebing and Pollak<sup>20</sup> determine iodine and chlorine by determining the sum of the halides gravimetrically and then determining the iodine on another portion of the sample by precipitation as palladous iodide. The same procedure can be used to determine iodine and bromine.

Bromine and chlorine are determined by weighing the mixed silver halides then dissolving in potassium cyanide and electrolyzing the silver.

<sup>18</sup> Sendroy, *J. Biol. Chem.*, 1937, **120**, 335.

<sup>19</sup> Moser and Miksch, *Zeits. für analyt. Chem.*, 1929, 293.

<sup>20</sup> Strebing and Pollak, *Mikrochemie*, 1925, **3**, 38.

## An Improved Horizontal Microburette

By A. LACOURT

*Microchemistry Centre, Brussels University.*

THE exact measurement of very small volumes of aqueous solution constitutes the greatest problem in microtitrimetric work. Taps, after-flow films, and calibration are responsible for most of the errors which arise. In this *Microchemistry Centre*, the horizontal burette of Benedetti-Pichler<sup>1</sup> has been used for some time, by every class of worker, and very good results have been obtained in a wide range of exercises. Students make and calibrate their own burettes from glass tubing of suitable diameter, depending on the precision desired. The results are quite satisfactory using anything from very fine thermometer tubing up to tubing of 3.5 mm. bore, provided that the tip is fine enough to ensure a regular and slow, reproducible rate of flow. One drawback has, however, been observed. The flow is only regular when the tip is very fine. When this is so, filling and cleaning the burette are laborious operations, and, in addition, any change in the position of the burette alters the reproducibility of the flow.

<sup>12</sup> Umhoefer, *Ibid.*, 1943, **15**, 383.

<sup>13</sup> Lacourt, *Mikrochemie*, 1935, **23**, 308.

<sup>14</sup> Thompson and Okidale, *J. A.C.S.*, 1930, **52**, 1,195; 1933, **55**, 1,292.

<sup>15</sup> Willard and Thompson, *Ibid.*, 1930, **52**, 1,893.

<sup>16</sup> B.I.O.S. Final Report No. 1606, Progress of Microchemistry in Germany.

<sup>17</sup> Elving and Ligett, *Ind. Eng. Chem. (An. Ed.)*, 1942, **14**, 449.

<sup>1</sup> Benedetti-Pichler, A. A., "Microtechnique of Inorganic Analysis" (New York), 1942.

Experiments were carried out using a vertical (ascending) capillary sealed between the horizontal one and the descending one. Such a capillary offers a certain resistance to the flow of liquid, helping to retain the liquid in the burette. The height of the intermediate capillary should not exceed the maximum capillary rise of water in such a tube. In practice, a 7- or 8-cm. tube, attached to the end of the horizontal capillary, is convenient, as shown in Fig. 1, for maintaining reproducible flow without necessitating the very narrow tip.

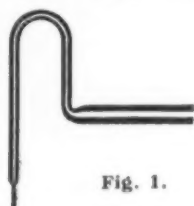


Fig. 1.



Fig. 2.

Fig. 1.—Construction of modified burette.  
Fig. 2.—Meniscus in wide-bore tubing.

The liquid flows as easily as before on contact with a liquid or glass surface, and the flow ceases on breaking contact. The pulsation-like phenomenon associated with the flow in the original burette is almost imperceptible in the improved type.

Calibration is best carried out using the titration of bi-iodate against thiosulphate. (For small burettes, with capacity less than 2 ml., it is better to calibrate with the

solutions for which the instruments are later to be used). Calibration of 180 scale units of such a burette, the bi-iodate being 0.1 N and the thiosulphate 0.1 N, gave values as follows: 1.003, 1.004, 1.002, 1.003, 1.003, 1.007, 1.006, 1.004, 1.003, 1.004, 1.005, 1.007, 1.005  $\mu$ l.

Great care must be taken in cleaning these instruments and in filling them with standard solution. Concentrated sulphuric acid or sulphuric-chromic mixture should not be used for cleaning, either water, alcohol or dilute nitric acid being more suitable. The instruments should be emptied, cleaned and dried after use, and never left partially filled overnight, even if they are going to be used for the same solutions the next day. Lack of reproducibility is likely to result if these precautions are neglected.

The home-made instruments are attached to a wooden board on which a paper millimetre scale is stuck. Volume values obtained from calibration are written on this paper.

With instruments of wider bore, the meniscus takes a somewhat different form from that usually obtained, but good reproducibility is obtained when the level is taken as shown in Fig. 2. However, when choosing glass tubing, preference should be given to the narrowest convenient bore, in order to get better accuracy in reading the horizontal scale of volumes.

Any quantitative work requiring the precise measurement of liquids can readily be carried out with the help of these microburettes.

## Miscellaneous Microchemical Devices\*

### XV—A Device for Testing Gases

By J. T. STOCK and M. A. FILL

Chemistry Department, L.C.C. Norwood Technical College, London.

THE device (Fig. 1) is constructed mainly from 2-mm. bore glass tubing and is suitable for attachment to a reaction vessel such as a 40 mm.  $\times$  8 mm. micro test tube. The test papers that are employed can be inserted or withdrawn in a moment.

Guide arm A, attached to gas tube B, is of glass rod of such diameter as to slide easily into cap C. A strip or circle of filter paper D, impregnated with a suitable reagent,<sup>1</sup> is gripped between the upper end of the gas tube and the end of the shorter branch of the cap. Gripping pressure is provided by a thin rubber band E stretched as shown. Gas penetrating the test paper escapes through the narrow annulus around the guide arm.

It is obvious that, to prevent leakage, the tube-ends gripping the test paper should be both flat and parallel. This is partially achieved by cutting as squarely and cleanly as possible. The two parts are then assembled and the rubber band is fitted. A small circle of copper sheet, both sides of which are armed with medium carborundum powder and oil, is then inserted in place of a test

paper, and is carefully rotated, releasing the pressure at intervals. When this treatment has rendered the tube ends parallel, polishing with fine carborundum is carried out in the same way.

The device works equally well on a larger scale of construction. In this form it has proved very useful in carrying out routine arsenic determinations by the Gutzeit method.

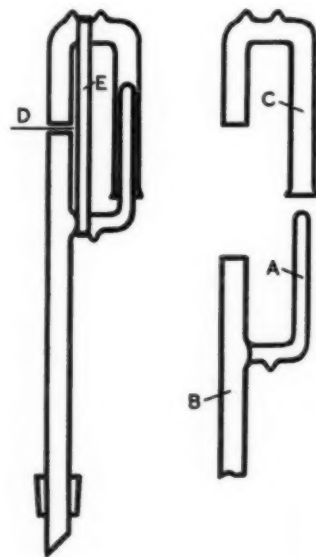
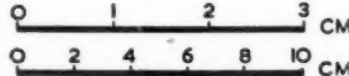


Fig. 1.—Gas-testing apparatus (upper scale, micro version; lower scale, larger version).



<sup>1</sup> See, for example, Whob, C. L., "An Introduction to Microchemical Methods," Methuen, London, 1938, p. 90; *ibid.*, *Analyst*, 1940, **65**, 405; Belcher, R., and Wilson, C. L., "Qualitative Inorganic Microanalysis," Longmans, London, 1946, p. 36.



## Evaluating Hydrogen Embrittlement in Acid Pickling

By M. Rosenfeld

**I**N acid pickling, two undesirable effects commonly recognised are: metal attack and hydrogen embrittlement. This article is concerned with the study of hydrogen embrittlement effects of solutions that readily remove rust, namely, 3.6 N sulphuric acid at 175° F. and 4.8 N hydrochloric acid at 77° F., both uninhibited and inhibited against metal attack.

The objectives of the investigation were:—

1. To determine the most satisfactory acid solution under the conditions indicated.

2. To improve available inhibitors so that detectable embrittlement could be avoided or converted to embrittlement readily removable by subsequent treatment.

3. To prepare inhibitors which would prevent observable embrittlement so that removal of hydrogen would not be necessary.

The standard tensile test was used in studying the extent of hydrogen embrittlement, since it enables rapid recognition of intense, partial, or absence of penetration of embrittlement. The per cent. reduction in area was used as a measure of the ductility and embrittlement of the material. Prevention of embrittlement refers to such prevention only in so far as it can be recognised by this test.

The study was restricted to three grades of cold finished steel: SAE 1020, SAE 1095 and molybdenum silicon steel. Pickling was performed separately for each specimen by inserting it into a vertically held test tube 1 in. in diam. and 15 in. long, followed by filling of the tube with a solution to submersion of the specimen. The pickling with hydrochloric acid solutions was for 90 min. at 77° F., and for other solutions 90 min. at 175° F. Preparation of specimens consisted of swabbing with naphtha followed by acetone and water washes and air-drying; the

after-pickling treatment was by water, then alcohol washes and air-drying.

Samples subjected to boiling after treatment were prepared and air-dried as above followed by a 10-min. boil, then water washed and subsequently alcohol washed and air-dried.

The commercial inhibitors are code designated as A, B and C. Letter D designates an inhibited water soluble pickling chemical.

With uninhibited sulphuric acid as the pickling bath, 61 to 69% of the ductility of SAE 1020 steel is lost, and except for a small core in the centre the rod fracture indicates embrittlement throughout.

Boiling identically treated rods for a period of 10 min. results in only 30 to 40% of the ductility of SAE 1020 steel being lost, restoring approximately 20% of the ductility. However, boiling does not improve the depth of embrittlement as shown by the fracture.

When 1% formaldehyde is added to the sulphuric acid pickling bath, 52 to 59% of the ductility of SAE 1020 steel is lost. The nature of the fracture is not essentially altered by the addition of formaldehyde; however, when identically treated rods are boiled in water for 10 min. the ductility is completely restored. The use of formaldehyde in uninhibited sulphuric acid pickling bath makes possible removal of embrittlement by boiling, giving the typical conical break characteristic of ductile specimens. The addition of 1% of quinoline to the sulphuric acid pickling bath produces results nearly identical to those obtained by formaldehyde.

With inhibited sulphuric acid as the pickling bath, using either commercial inhibitors C or A, 52 to 57% of the ductility of SAE 1020 steel is lost. It will be noticed that, just as in the case of uninhibited sulphuric acid, the fracture indicates embrittlement

throughout the rod, except for a small core in the centre.

Boiling identically treated rods for a period of 10 min. results in only 20 to 26% loss in ductility, but depth of embrittlement is not improved.

A very special effect occurs when p. toluidine 0.05 Molar plus 1% formaldehyde is used as the inhibitor in the sulphuric acid bath. Embrittlement of SAE 1020 steel is completely avoided so that subsequent boiling is unnecessary.

With uninhibited hydrochloric acid (4.8N) at 77° F. as the pickling bath, 60 to 70% of the ductility of SAE 1020 steel is lost. This is not essentially different in amount from that obtained with uninhibited 3.6 N sulphuric acid at 175° F. That the two are not identical is shown not only by the fractures, where it is seen that depth of embrittlement is much less than with the sulphuric acid, but also by the effect of subsequent treatment with boiling water.

Boiling identically treated rods of SAE 1020 steel for a period of 10 min. results in complete removal of embrittlement.

By adding 1% formaldehyde to the hydrochloric acid pickling bath it might appear that complete prevention of embrittlement has occurred. However, close inspection of the specimens reveals surface cracks not clearly seen in the photographs.

With inhibited hydrochloric acid as the pickling bath, using commercial inhibitors A or B on SAE 1020 steel, 19 to 27% of the ductility is lost. The fracture visually appears different from that of the inhibited sulphuric acid.

Boiling identically treated rods of SAE 1020 steel for a period of 10 min. results in complete restoration of ductility. This is not surprising, in view of the fact pointed out above that pickling SAE 1020 steel in the uninhibited 4.8 N hydrochloric acid gives no embrittlement if the pickled rod is subsequently boiled in water for 10 min.

With 1% quinoline plus 1% formaldehyde as the inhibitor in the 4.8 N hydrochloric acid pickling bath at 77° F., complete prevention of hydrogen embrittlement is obtained. A

From *Iron Age*, June 17, 1948, p. 82-87.

# Perhaps we're prejudiced but to us these parts are greater than the whole



"VISIBILITY — GOOD". Whatever the weather the efficient action of these zinc alloy die castings enables motorists to see ahead. For they comprise the casing for the mechanism of a windscreen wiper.\*

#### Why the parts are zinc alloy die cast

The main casting provides a base for the motor assembly, which drives a shaft passing through a central boss to the gearing and crank mechanism in the deeper half of the casting. Bronze inserts for the bearings are held in the die by means of necked projections which are subsequently broken off. The die casting process enables the lettering and switch details to be incorporated on the casing as a permanent feature.

#### Other car equipment too

The modern car contains scores of zinc alloy die castings. Com-

ponents generally made — in whole or part — by zinc alloy die casting include stressed parts in the chassis (such as shock absorber bodies), bumper parts, carburettors, petrol pumps, radiator grilles, electrical fittings, number plates, car radio parts and door hardware.

#### Some facts about zinc alloy die casting

Speed of production is an outstanding feature of the die casting process — the shortest distance between raw material and finished product. Zinc alloys are the most widely used of all metals for die casting because they yield castings with the following qualities :

**STRENGTH :** Good mechanical properties for stressed components.

**ACCURACY :** Castings can be made practically to finished dimensions and need little or no machining.

**STABILITY :** Close tolerances are maintained throughout the life of the casting.

These are the properties which accounted for the widespread wartime use of zinc alloy die casting in the quantity production of such things as fuses, gun sights, periscopes and tank carburettors.

#### British Standard 1004

Alloys conforming to B.S. 1004 should be specified for all applications where strength, accuracy and stability are essential.

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\* Reproduced approximately full size by courtesy of Joseph Lucas Ltd.

chemical reaction occurs and one of the products is thought to be the formaldehyde addition compound of dihydroquinoline. Reduction of strength of quinoline and formaldehyde from 1% each to 0.2% of each in 4.8 N hydrochloric acid does not alter its effectiveness in prevention of hydrogen embrittlement. Quinoline alone added as an inhibitor to 4.8 N hydrochloric acid is seen to be quite ineffective.

Another highly effective inhibitor of hydrogen embrittlement on SAE 1020 steel in the 4.8 N hydrochloric acid at 77° F. is the 0.05 Molar p. toluidine plus 1% formaldehyde mix. The complexes obtained have been subjected to much study and well reviewed by Sprung. This mix has been shown earlier in this paper to be effective in the sulphuric acid. However, in hydrochloric acid (4.8 N) at 77° F. this acts as an inhibitor of metal attack as well, which is not true in the case of sulphuric acid.

If formaldehyde in concentrations of 0.2% or 1% is added to 4.8 N hydrochloric acid inhibited with commercial inhibitor B, complete prevention of embrittlement of SAE 1020 steel is obtained. Adding 1% quinoline to 4.8 N hydrochloric acid pickling bath inhibited with commercial inhibitor B, on the other hand, offers no advantage;

26 to 33% loss in ductility of SAE 1020 steel occurs.

Pickling agent D used at 175° F., without additional acid, has about the same effect as the sulphuric acid studied, in that embrittlement occurs, not removable by subsequently boiling the SAE 1020 steel rods in water, but removable if 1% formaldehyde is added and the rod is subsequently boiled in water for 10 min.

The SAE 1095 steel was tested with 4.8 N hydrochloric acid as the pickling bath at 77° F., using some of the inhibitors found to be effective as a result of the work on SAE 1020 steel. It was found that addition of formaldehyde from 0.2% to 1% to commercial inhibitor B or quinoline-formaldehyde mixes containing 0.2% each to 1% each were completely effective in preventing embrittlement of this high carbon steel.

The molybdenum silicon steel contained 0.52 C, 0.82 Mn, 0.013 P, 0.018 S, 2.04 Si, 0.10 Cu, 0.17 Ni, 0.27 Cr and 0.33 Mo.

Studies were made with 4.8 N hydrochloric acid as the pickling bath, using the same inhibitors as in the case of the SAE 1095 steel. Prevention of embrittlement was obtained in all cases. All studies were confined to 77° F.

aviation and automotive companies, and manufacturers of diesel and stationary engines. Lead-indium bearings have also found application in machine tools.

Whereas the lead-indium plating of bearings for aircraft engines exemplifies the dual handling of corrosion and high stresses developed through continuous running of the machine, the problem of extremely high-bearing pressures is featured in a Navy landing gear equipment installed on aircraft carrier flight decks.

The bearing pressure developed during sudden braking of the aircraft is very high, of the order of 10,000 psi., at which pressure conventional pressure lubrication is rendered inoperative.

The frequent seizure of the sheave bearing and the scoring of the bronze surface of the bearing led the Navy to consider possibilities of a solution by lead-indium plating.

Best results were obtained through the use of silver-lead-indium coatings applied electrolytically in sequence and alloyed by heating. Bronze bearings treated in this fashion provided a superior service, and hundreds of these bearings have been made for the Navy.

### Types of Baths

The controls and specifications of lead-indium plating are very rigid. As is true with all general plating, freedom of the base metal from dirt, grease and oxide film is essential. At American Airlines' main overhaul base, a deposition test of the indium bath is made each day of use. An analysis is carried out weekly.

There are four types of baths for indium plating which have been used commercially with varying degrees of success. These can be divided into the solution bath and the bath requiring indium anodes for replenishment.

The solution bath is a clear indium cyanide plating bath which is free from sludge and of high alkalinity. It is available in concentrated form and it is only necessary to dilute the concentrate with an equal amount of water in preparation of the bath. This procedure can be followed in the replenishment of the bath as it is expended.

The current density for the cyanide bath is 15-20 amp./sq. ft. For the anodes, plain steel is preferred to stainless steel, carbon or platinum. The latter anodes tend to catalyze the oxidation of organic matter, which increases the possibility of sludging. The bath is kept at room temperature, with or without agitation. The cathode

## Indium Plated Lead Bearings Withstand High Stresses

By Joseph Albin

SOME of the characteristics of lead which make it suitable as a bearing metal are considerably improved by small additions of indium. The indium deposited and subsequently diffused into the underlying coat makes the bearing surface harder and tougher, as well as more resistant to corrosion by the lubricant.

Lead-indium plating normally goes over a silver base which in itself is supported by a steel shell. Silver has the internal properties which resist failure due to fatigue. To make up for the lack of "oiliness" needed in a good bearing surface, a thin layer of lead is electro-deposited over the silver surface. Lead, however, is soluble in organic compounds present or formed in lubricating oils with rises in temperature due to engine operation. To

prevent the corrosion of the bearing surface and to permit the surface to retain its oil film more completely by increasing its wettability, a thin or practically flash coating of indium is electro-deposited and heat processed.

Hardening of the lead is accomplished by the diffusion of the indium. Addition of 4-6% indium markedly changes the relatively large crystalline structure of lead to that of a finely-furrowed appearance. On the Brinell scale, 8% of indium increases hardness from 3.11-7.28. The addition of 1% increases tensile strength from 1,600-3,000 psi.

While the majority of aviation bearings are silver-lead-indium, other metals onto which indium can be plated and diffused are copper, cadmium, zinc and tin. Much experimental work and testing has been done on this series of indium bearings by

From *Materials and Methods*, June, 1948, pp. 88-89.



efficiency is about 75%. Throwing power—excellent. Control of the solution is by analysis for cyanide and metal.

The baths requiring an indium anode for replenishment are as follows:

(a) *Sulphate bath*—contains about  $2\frac{1}{2}$  oz. of indium in solution per gal. The sodium sulphate content is about  $3\frac{1}{2}$  oz. per gal. The pH of the solution is between 2.0 and 2.5. Current—20 amp./sq. ft.

(b) *Fluoborate bath*.—Concentrated solutions of indium fluoborate are diluted with proper proportions of water. The bath is stable as long as a slight excess of fluoboric acid is present. The pH of the bath is approximately 0. and 0.2. Operation temperature—between 75° and 90° F. A current density of 100 amp./sq. ft. is employed.

(c) *Sulphamate bath*.—Operates satisfactorily with  $2\frac{1}{2}$  oz. of indium metal per gal. The current density is as high as any bath and is not critical. The indium content is

supplied by indium anodes, and the efficiency of the bath is maintained by control of the pH and the indium content.

After the plating of indium, the second phase in order to secure the full values of the deposit, is to have the indium diffused into the base metal. This is done by placing the plated part in an oven or hot bath and subjecting it to 2 hours of heat-treatment at a point slightly above the melting point of indium. As indium melts at 311° F., the diffusion should be carried out at about 350° F. This process may be shortened by increasing the temperature, but only after the diffusion has actually begun. Failure to observe the proper temperature at the beginning of the diffusion process may lead to the formation of surface bubbles.

The amount of indium used is extremely small, and in most cases does not exceed 5 milligrams/sq. in. The thickness of the undercoating will vary from a few ten-thousands to one or two

thousands of an inch. The thickness of indium deposit depends on surface requirements.

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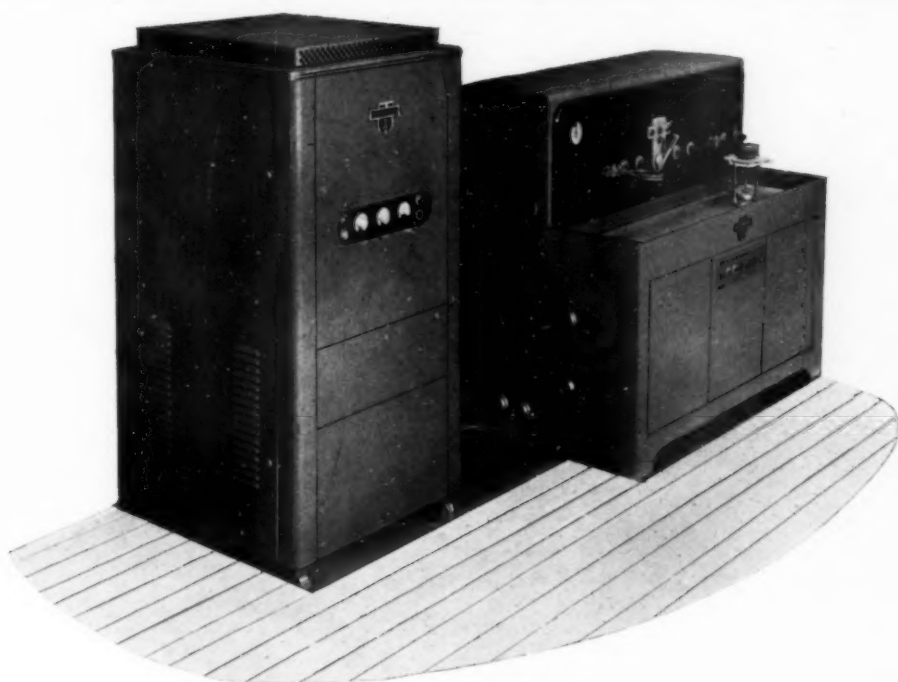
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